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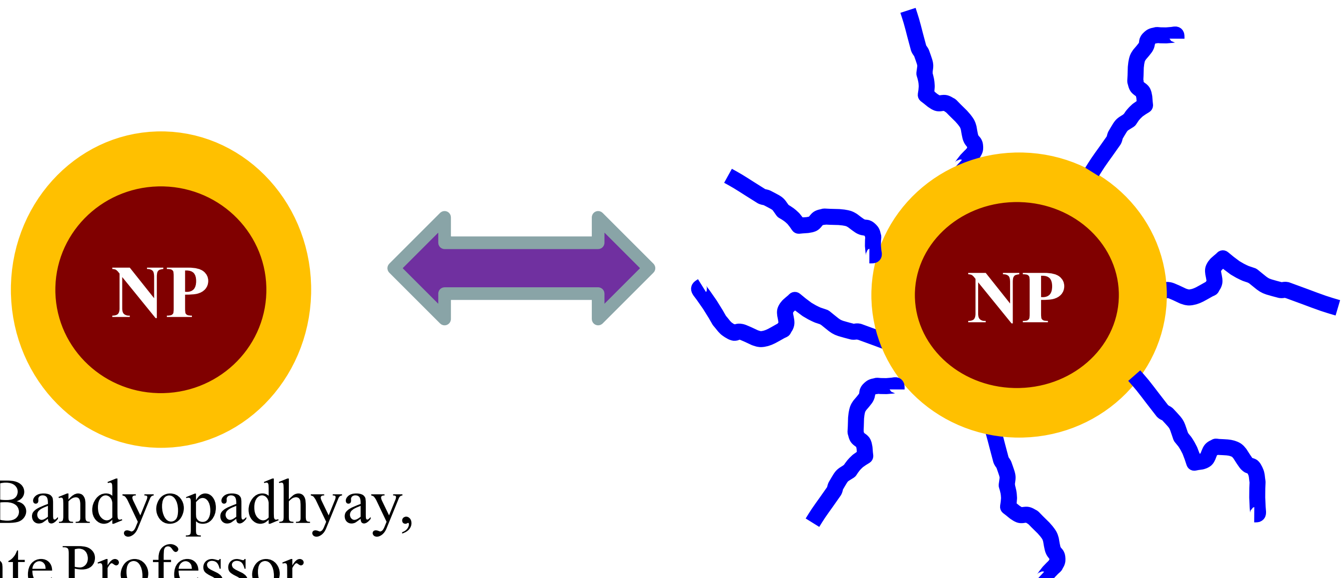
Synthesis and Functionalisation of Nanoparticles



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NTNU
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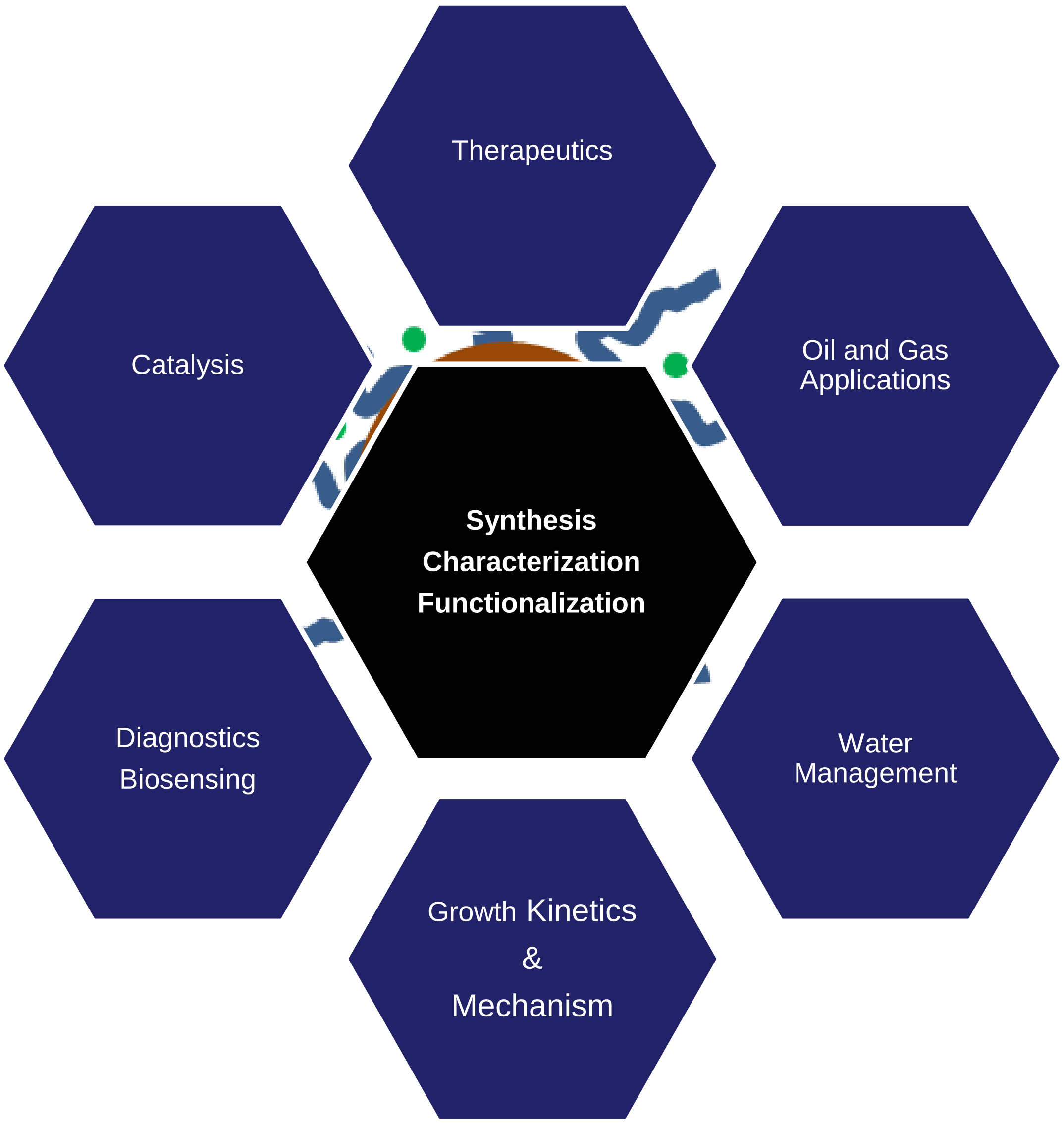

Therapeutics
Catalysis
Oil and Gas Applications
Synthesis
Characterization
Functionalization
Diagnostics
Biosensing
Water Management
Growth Kinetics
&
Mechanism

Reading Material

- Fabrication and Application of Nanomaterials, S. Bandyopadhyay, McGraw-Hill Education.

- Mora-Huertas, C. E., Fessi, H., & Elaissari, A. (2011). ***Advances in colloid and interface science***, *163*(2), 90–122.

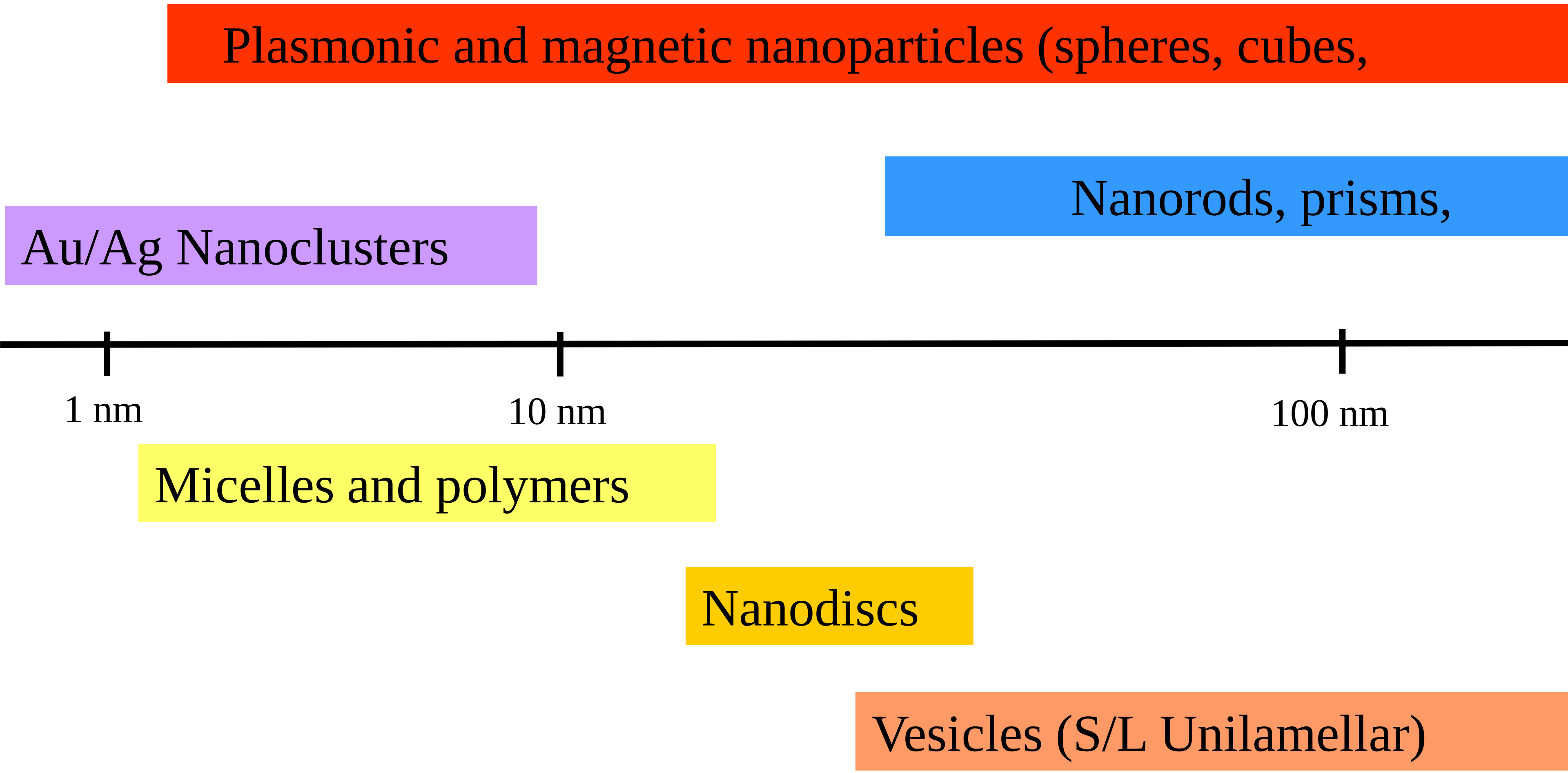
- Bally, Florence, et al.(2012) ***Polymer****,* 53(22), 5045-5051.

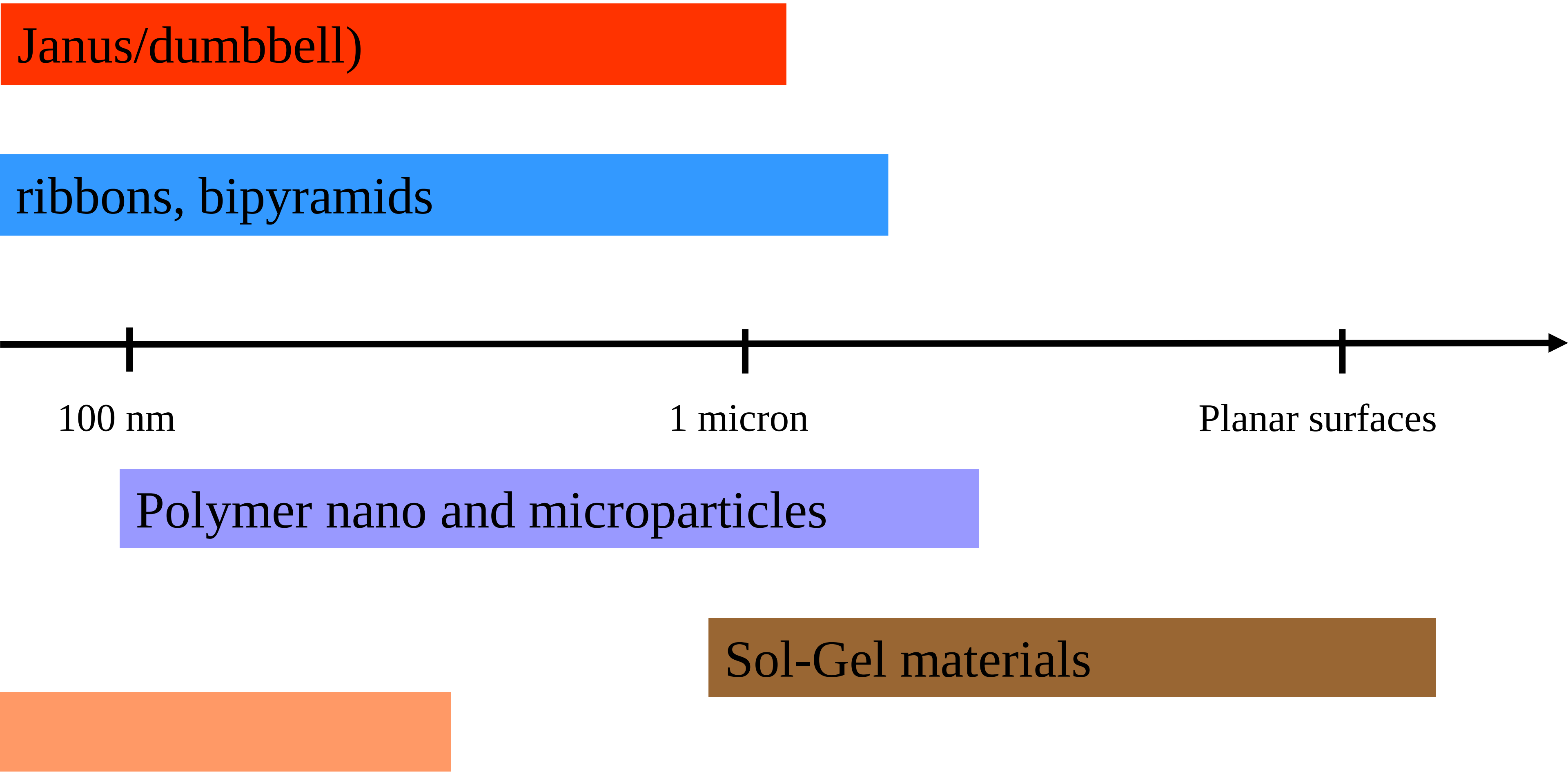
- Saad, Walid S., and Robert K. Prud’homme. (2016) ***Nano Today,*** 11(2), 212-227.

Topics

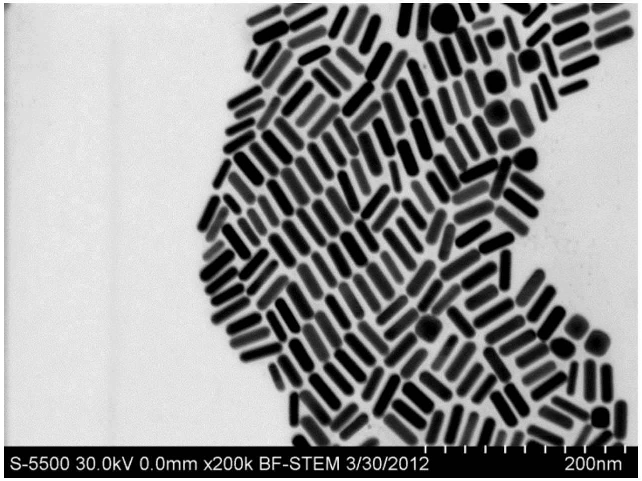
- **Metallic NPs**
  - Synthesis Methods
    - Reduction of Metallic Precursors
    - Thermal Decomposition
    - Colloidal Templating
    - One pot methods
  - Anisotropic NPs
- **Functionalization of NPs**
- **Polymer-based NPs**
  - Nanoprecipitation
  - Flash Nanoprecipitation
  - Precipitation Polymerization

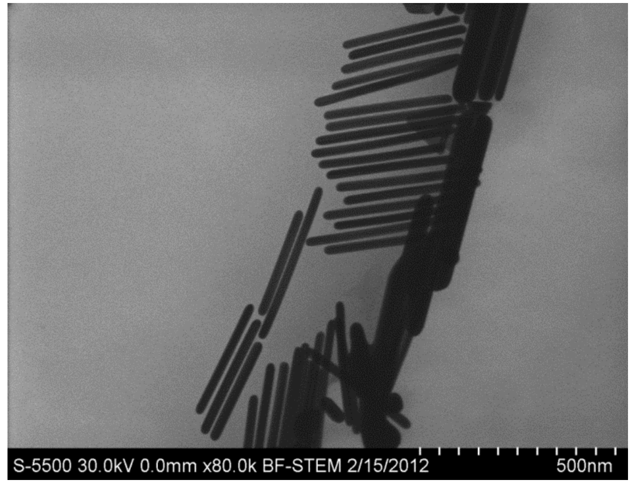
Nanomaterials

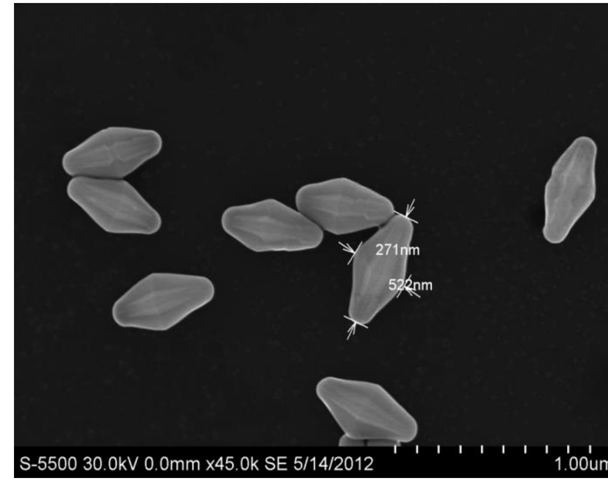


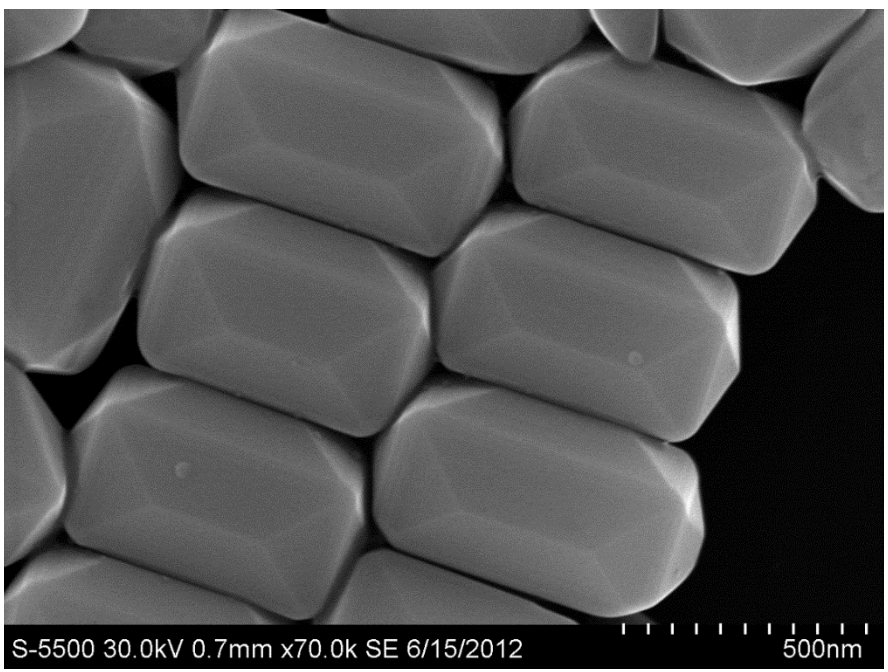

Janus/dumbbell)
ribbons, bipyramids
100 nm
1 micron
Planar surfaces
Polymer nano and microparticles
Sol-Gel materials

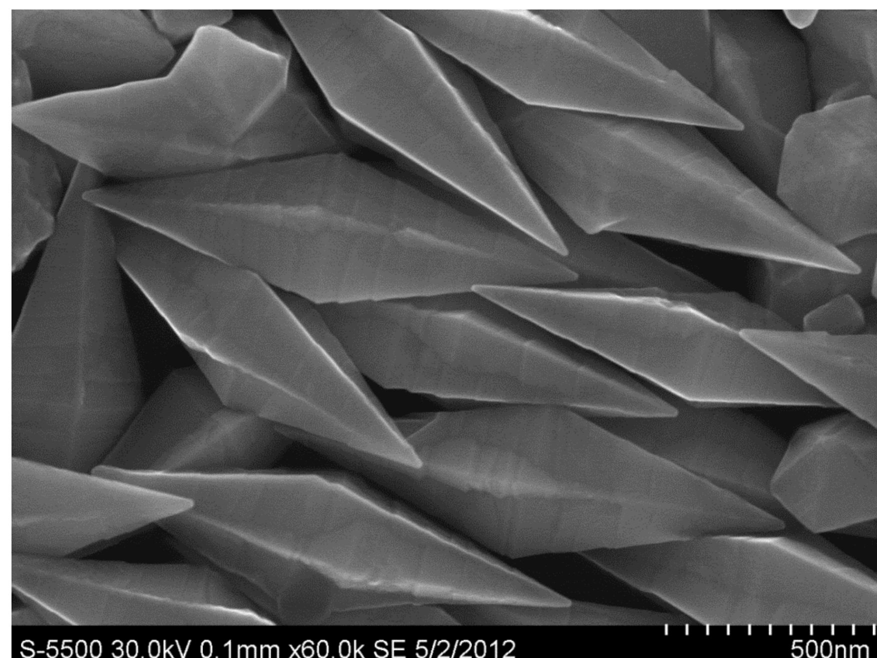
Library of NPs



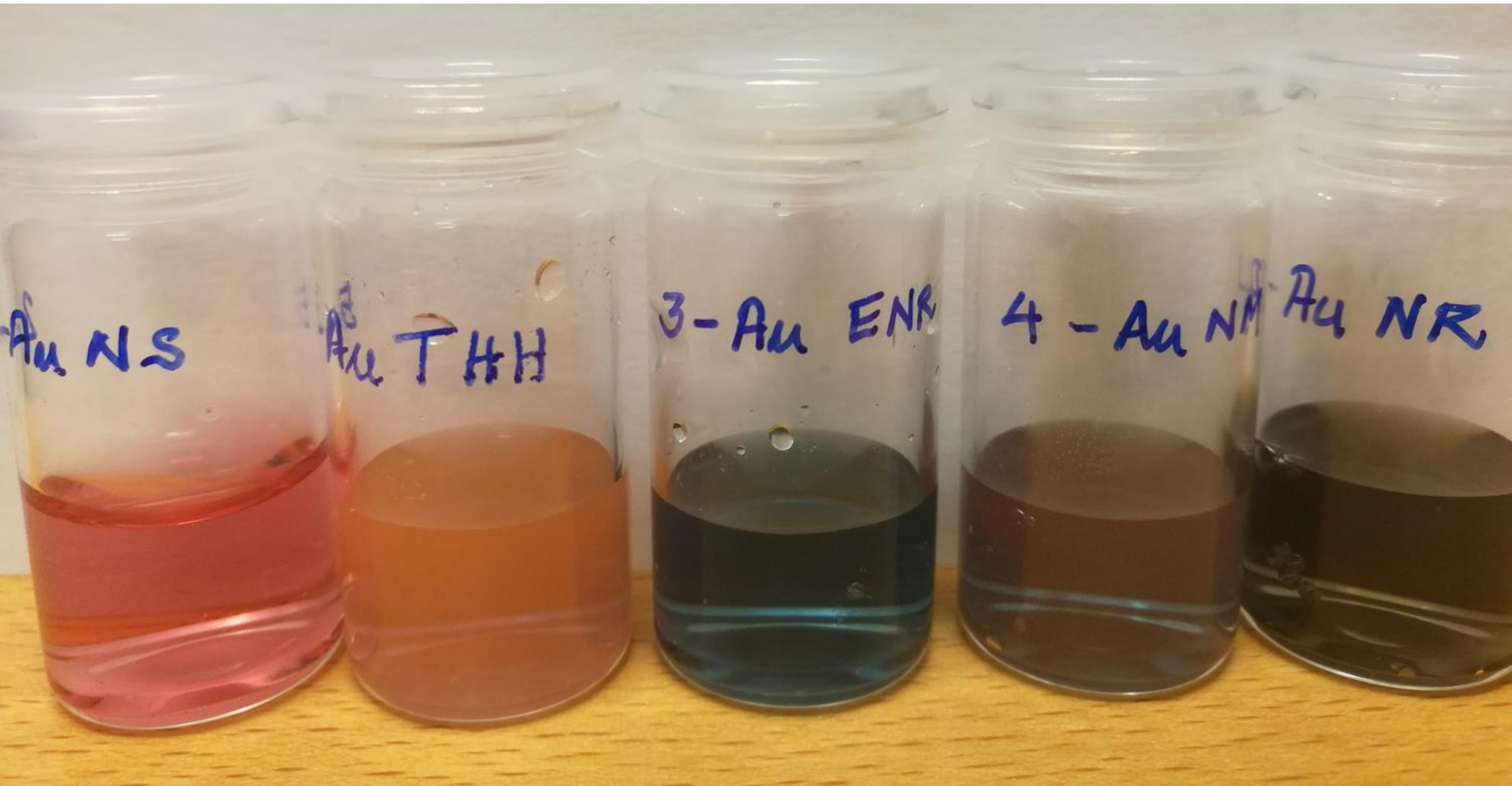




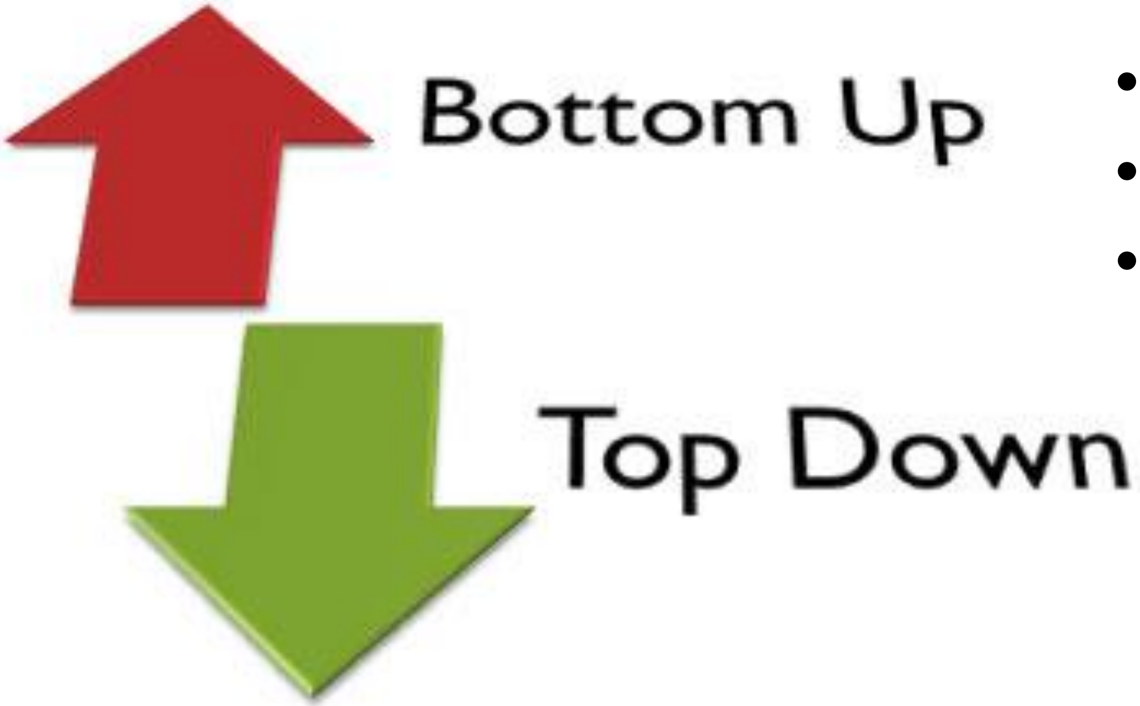




Synthesis of Metallic NPs



Synthesis Approaches



- Heterogeneity
- PSD
- Defects, Impurities

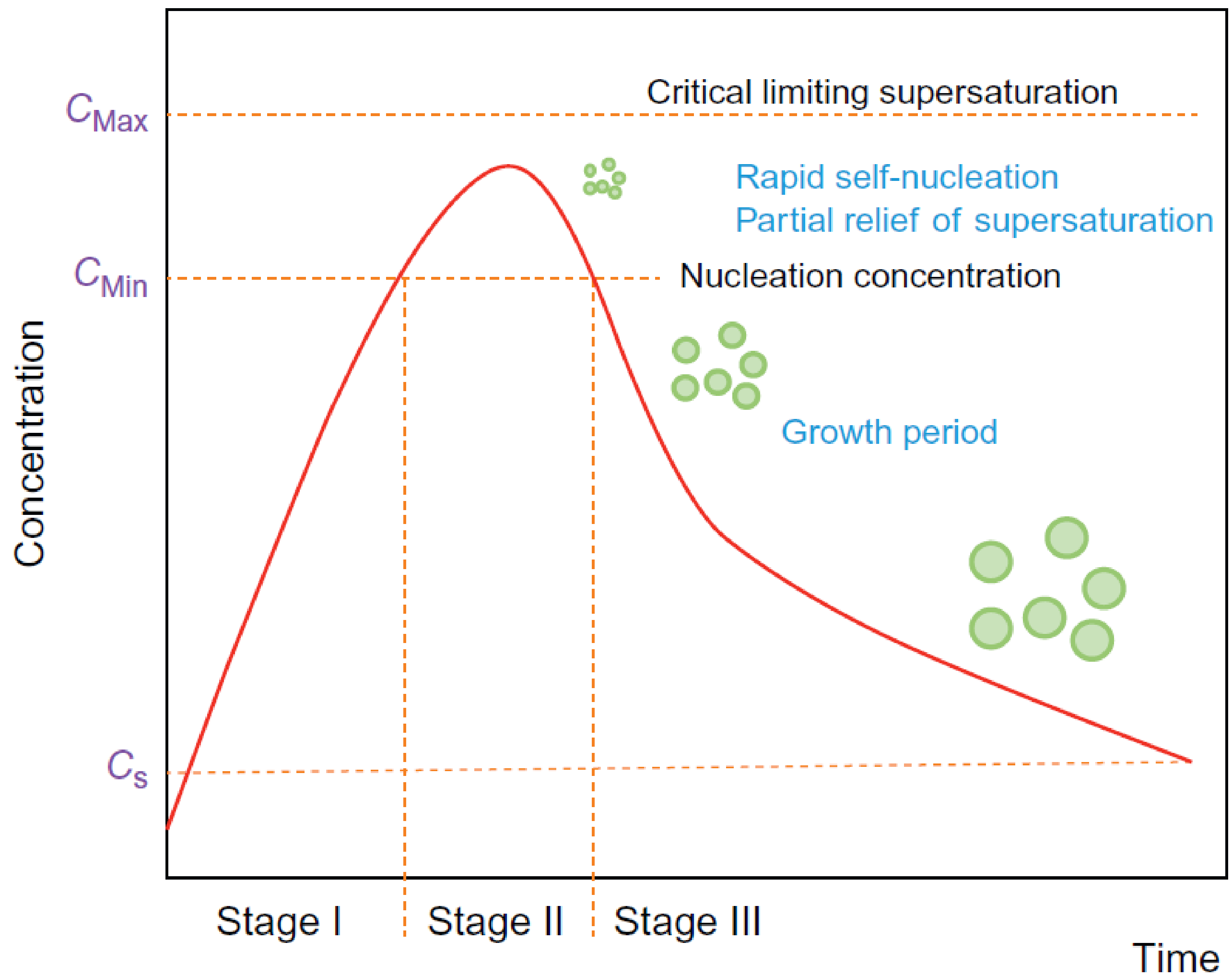
Classical Nucleation Theory

1. Supersaturation
2. Nucleation
3. Crystal growth
4. Secondary growth

$$S = \frac{c}{c*}$$

$$\sigma = \frac{\Delta c}{c*} = S - 1$$

Lamer's Diagram



Crystallization

&

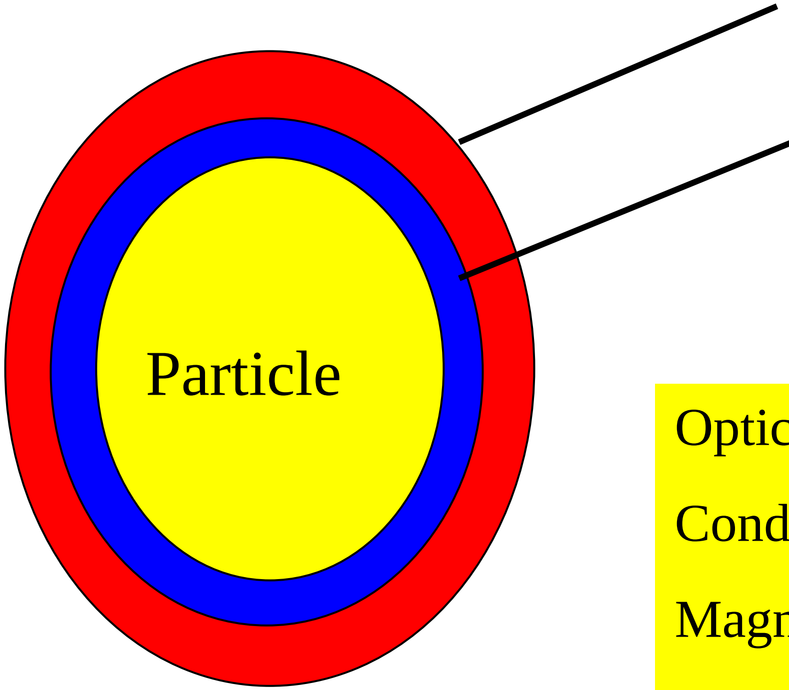
Precipitation

Crystallization FOR DUMMIES

1. Metal precursor
2. Reducing agent
3. Passivating ligand

Why?

Properties of Metallic NPs



Material Properties

Passivating ligand layer

- Optical properties
- Conductivity
- Magnetism
- Catalytic activity

- Refractive index
- Polarity/solubility
- Charge
- Functionality

Functionality/application

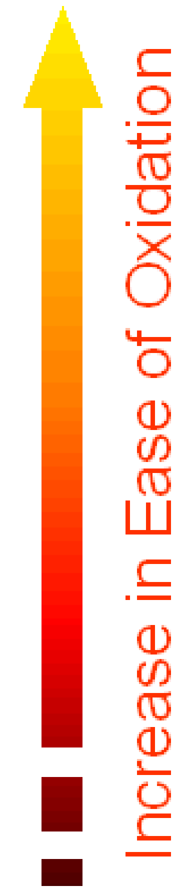
Rule of Thumb

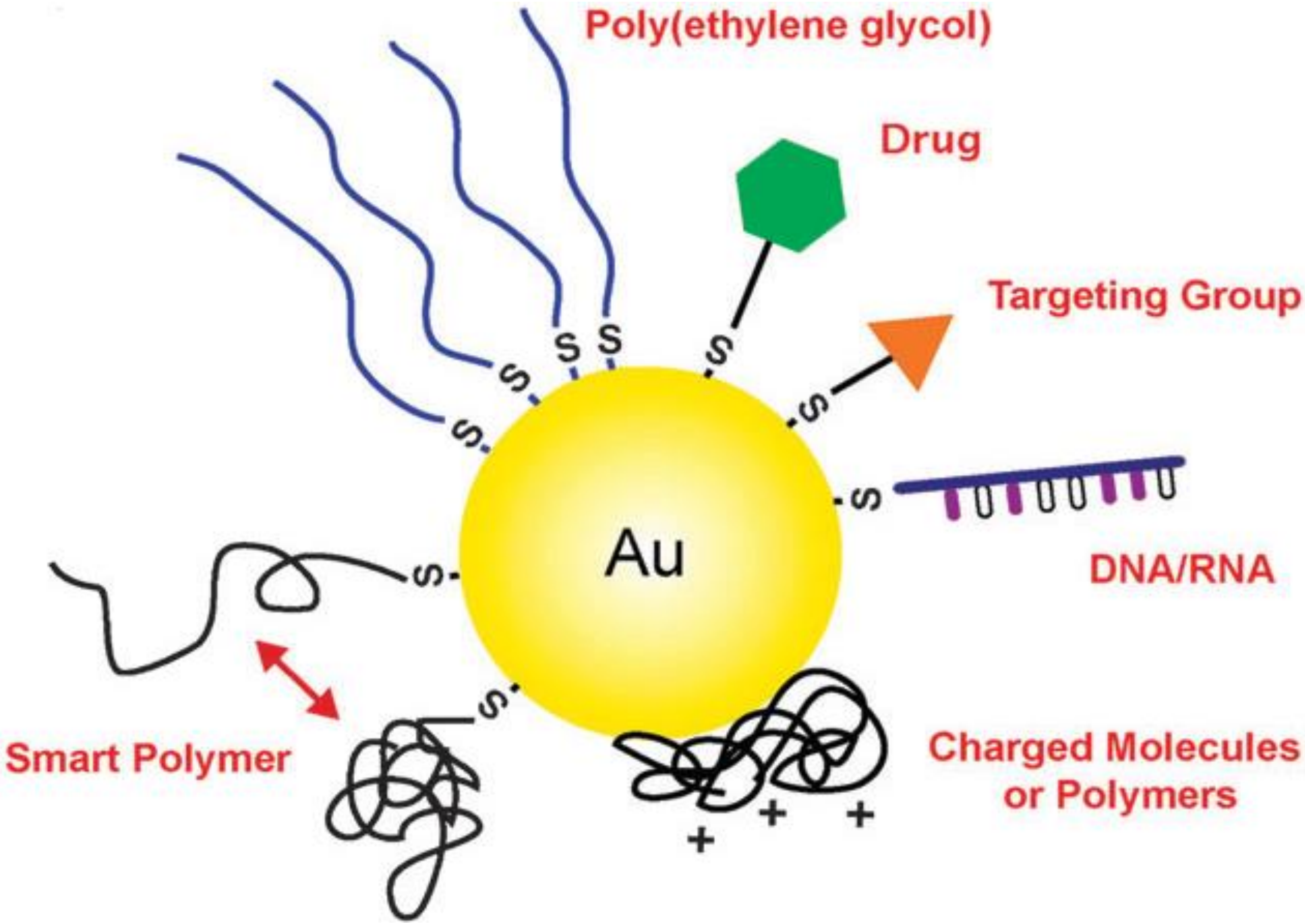
Redox potential

$$\propto^{-1}$$

Particle Size

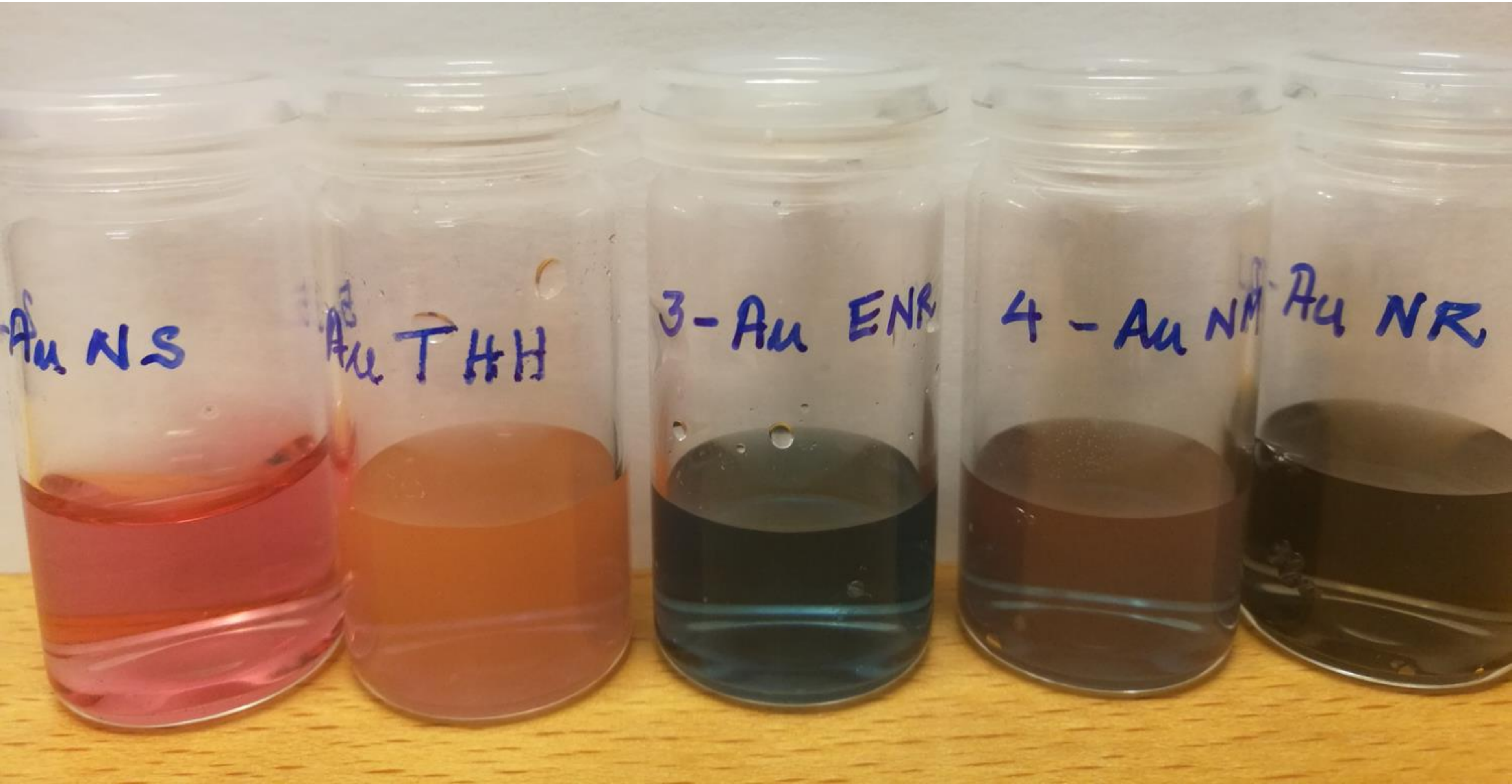
Metal	Oxidation Reaction
Lithium	$Li \rightarrow Li^{+} + e^{-}$
Potassium	$K \rightarrow K^{+} + e^{-}$
Barium	$Ba \rightarrow Ba^{2+} + 2e^{-}$
Calcium	$Ca \rightarrow Ca^{2+} + 2e^{-}$
Sodium	$Na \rightarrow Na^{+} + e^{-}$
Magnesium	$Mg \rightarrow Mg^{2+} + 2e^{-}$
Aluminum	$Al \rightarrow Al^{3+} + 3e^{-}$
Zinc	$Zn \rightarrow Zn^{2+} + 2e^{-}$
Chromium	$Cr \rightarrow Cr^{3+} + 3e^{-}$
Iron	$Fe \rightarrow Fe^{2+} + 2e^{-}$
Cobalt	$Co \rightarrow Co^{2+} + 2e^{-}$
Nickel	$Ni \rightarrow Ni^{2+} + 2e^{-}$
Tin	$Sn \rightarrow Sn^{2+} + 2e^{-}$
Lead	$Pb \rightarrow Pb^{2+} + 2e^{-}$
Hydrogen	$H_2 \rightarrow 2H^{+} + 2e^{-}$
Copper	$Cu \rightarrow Cu^{2+} + 2e^{-}$
Silver	$Ag \rightarrow Ag^{+} + e^{-}$
Mercury	$Hg \rightarrow Hg^{2+} + 2e^{-}$
Platinum	$Pt \rightarrow Pt^{2+} + 2e^{-}$
Gold	$Au \rightarrow Au^{3+} + 3e^{-}$



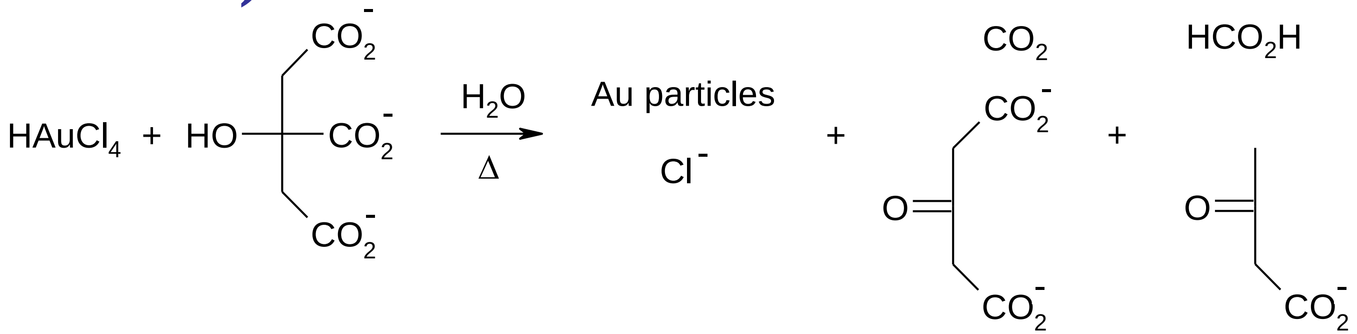


Xia, Y. et al., *Chem Soc Rev*, **2011**, 44-56

1. Reduction of Metallic Precursors in Solution



Turkevich Reaction (Citrate Reduction of Chloride Precursor)



- Aqueous phase synthesis
- Citrate acts both as reducing agent and passivating ligand
- Most common synthesis method (commercially available)
- Synthesis temperature typically 100 °C with refluxing conditions

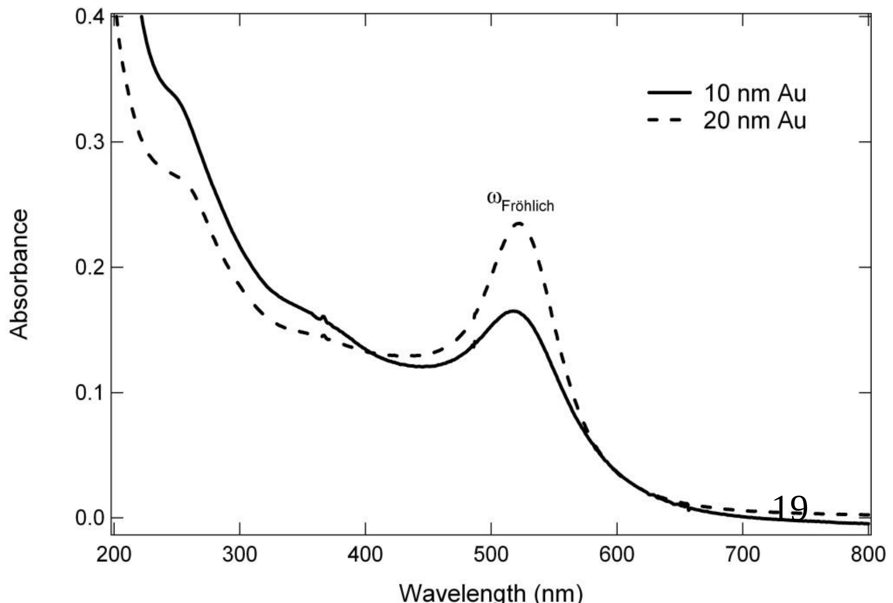
Turkevich, J. et al., *Discussions of the Faraday Society*, **1951**, 55-&

Turkevich, J. et al., *J. Phys. Chem.*, **1953**, 57, 670-673

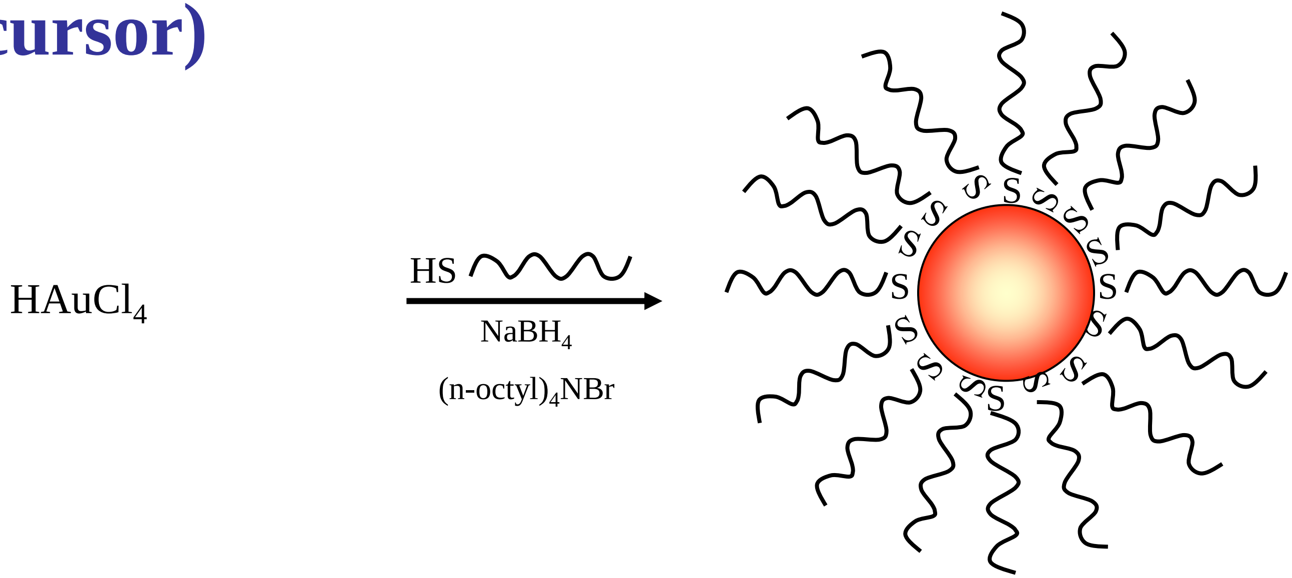
Turkevich, J. et al., *J. Colloid Sci.*, **1954**, 9, S26-S35

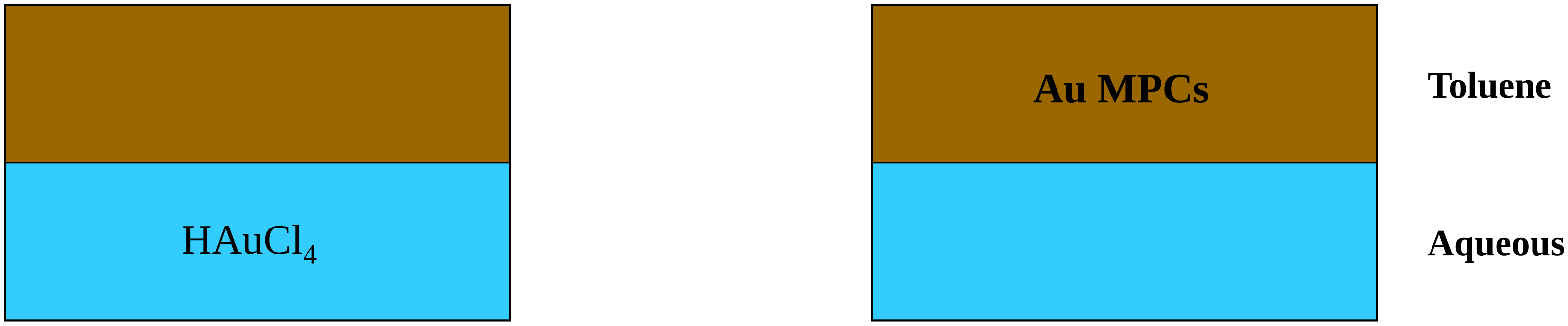
Turkevich Reaction

- Readily available in sizes from 2-200 nm
- Wide array of surface functionalities available by simple ligand exchange reactions
- Citrate can be displaced by thiols, isothiocyanates and phosphines
- Susceptible to flocculation/aggregation by changes in solvent conditions



Brust Reaction (BH_4^- Reduction of Chloride Precursor)





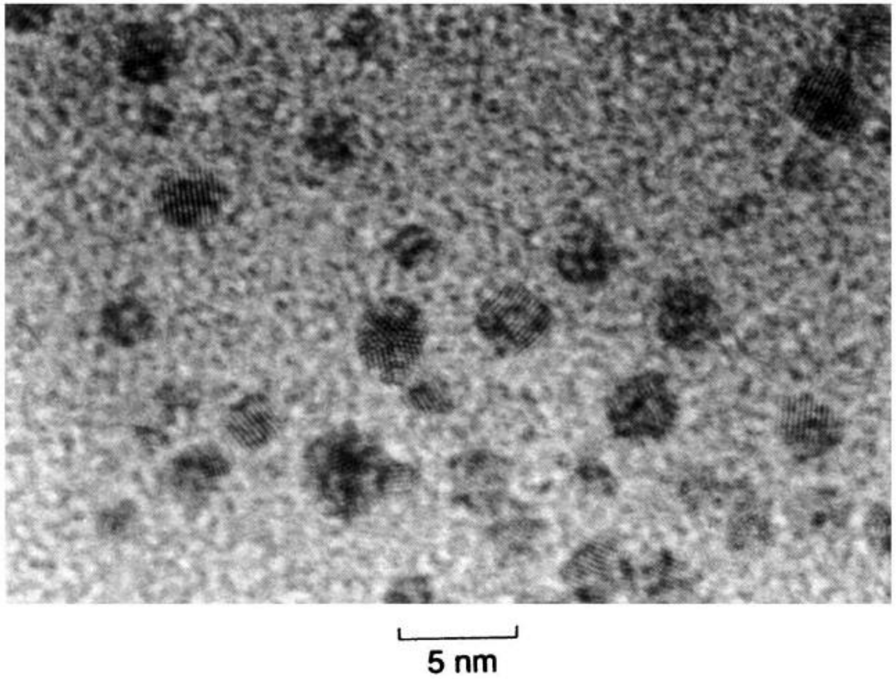
Brust, M. et al., *Chem. Commun.*, **1994**, 801-802

Brust, M. et al., *Chem. Commun.*, **1995**, 1655-1656

Brust Reaction

$AuCl_4^-{}_{(aq)} + N(C_8H_{17})_4 + (C_6H_5Me) \rightarrow N(C_8H_{17})_4 + AuCl_4^-(C_6H_5Me)$ (1)

$m AuCl_4^-(C_6H_5Me) + n C_{12}H_{25}SH(C_6H_5Me) + 3\, m e^- \rightarrow 4m Cl^-{}_{(aq)} + (Au_m)(C_{12}H_{25}SH)_n(C_6H_5Me)$ (2)



- Typically 1.5-8 nm particle size
- Very stable NPs.
- Access to a wide variety of surface functionalities through ligand exchange.
- Both polar and non-polar solvents.

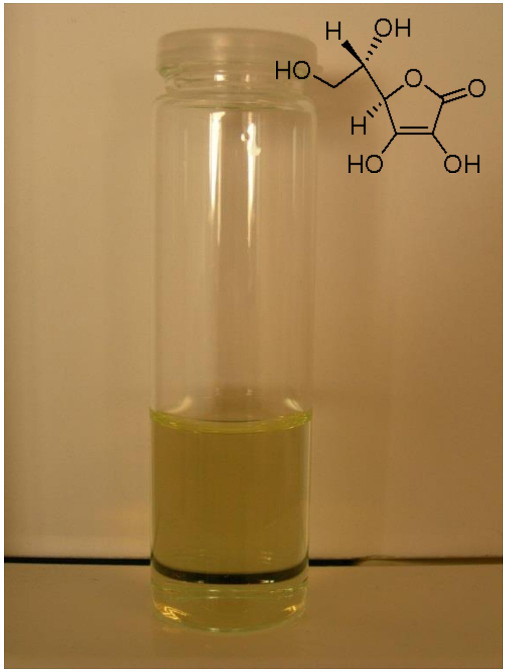
Brust, M. et al., *Chem. Commun.*, **1994**, 801-802

Brust, M. et al., *Chem. Commun.*, **1995**, 1655-1656

Goia reaction (Iso-ascorbic Acid Reduction of Chloride Precursor)

Reduction of auric acid with iso-ascorbic acid;

$$2\ HAuCl_4 + 3\ C_6H_8O_6 \rightarrow 2\ Au^0 + 3\ C_6H_6O_6 + 8\ HCl$$



Andreescu, D., Sau, T.K. and Goia, D.V., *J. Colloid Interface Sci.*, **2006**, 298, 742-751

Goia Reaction

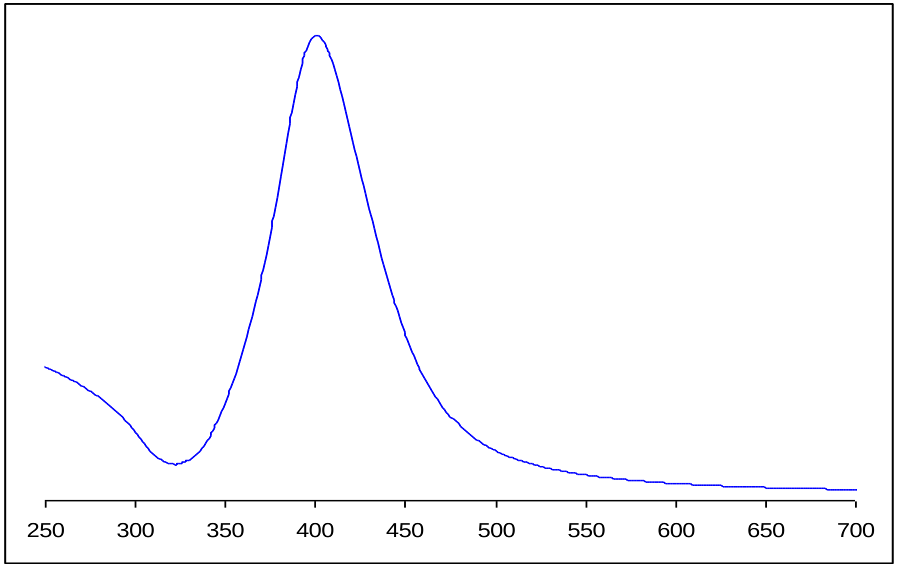
- *Stabilizer-free* meaning ascorbic acid acts as passivating ligand as for citrate
- Room temperature, very rapid nucleation and growth
- Aqueous phase synthesis
- Ascorbic acid can be displaced from surface by thiols etc.
- Particle size tunable through pH, reactant ratios, concentration
- 30-100 nm if ”stabilizer free” system at room temperature
- 80 nm to 5 μm if prepared in the presence of gum arabic at very high Au conc.

***Stabilizer-free* Goia reaction standard together with Turkevich particles.**

Andreescu, D., Sau, T.K. and Goia, D.V., *J. Colloid Interface Sci.*, **2006**, 742-751

Goia, D.V., Matijevic, E., *Colloids and Surfaces A*, **1999**, 139-152

Goia Reaction



- Reduction of silver nitrate by iso-ascorbic acid
- Slightly larger particles (40-70 nm)
- pH must be above 10

Co-Precipitation

- Metal salt precursors in aqueous solutions.
- Addition of a reducing agent (base).
- The products are generally insoluble species formed under conditions of high supersaturation.
- Nucleation is a key step, and a large number of small particles will be formed.
- Secondary processes, such as Ostwald ripening and aggregation, dramatically affect the size, morphology, and properties of the products.
- The supersaturation conditions necessary to induce precipitation are usually the result of a chemical reaction.

Co-Precipitation

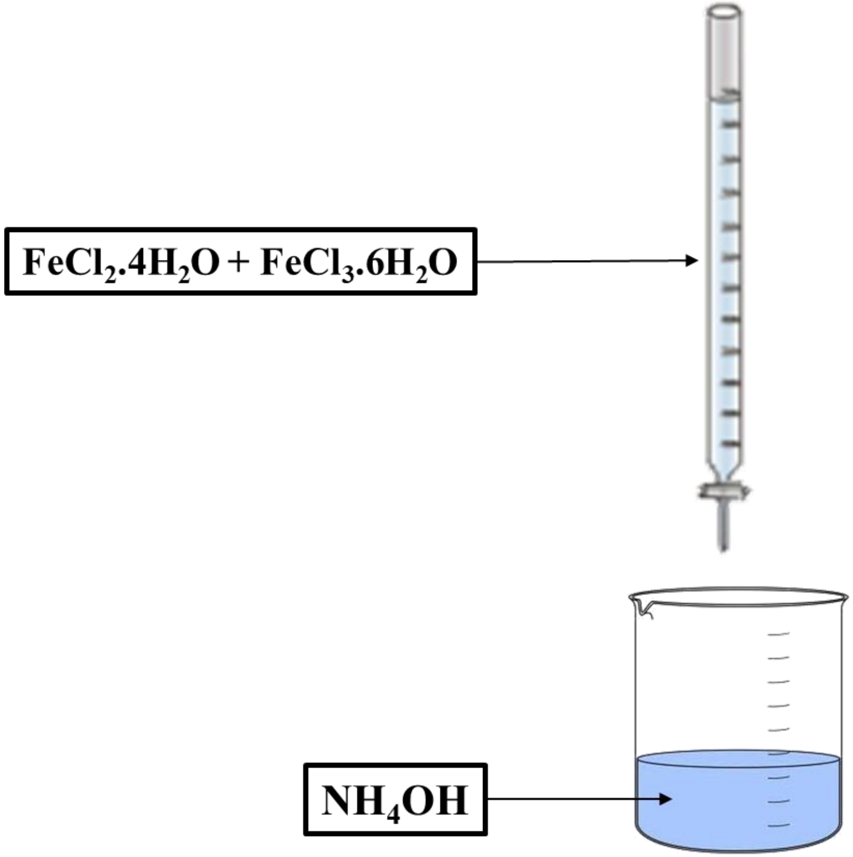
Advantages

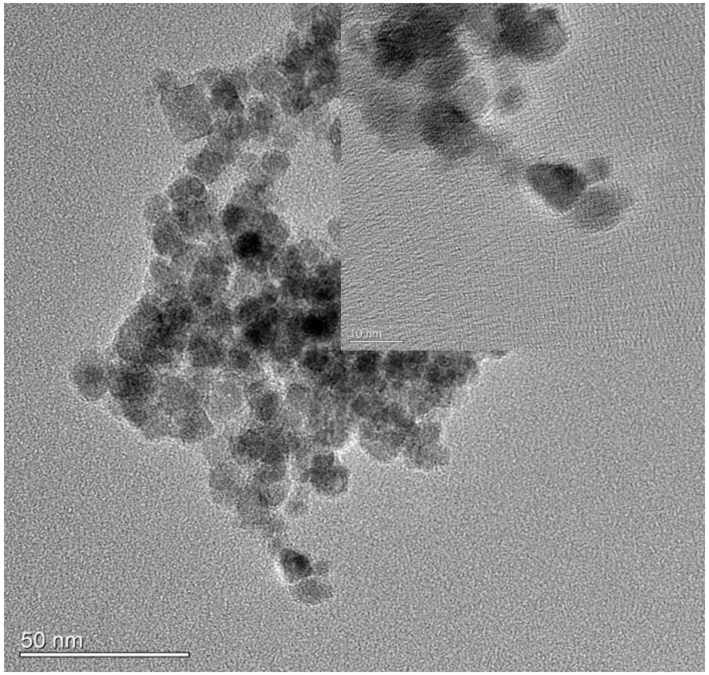
- Simple and rapid preparation
- No toxic intermediates
- No use of organic solvents
- Does not require precursor complexes
- Proceeds at low temperatures
- Scalable
- Reproducible

Disadvantages

- Particles with a broad size distribution.
- Trace impurities can also get precipiated with product.

Co-Precipitation

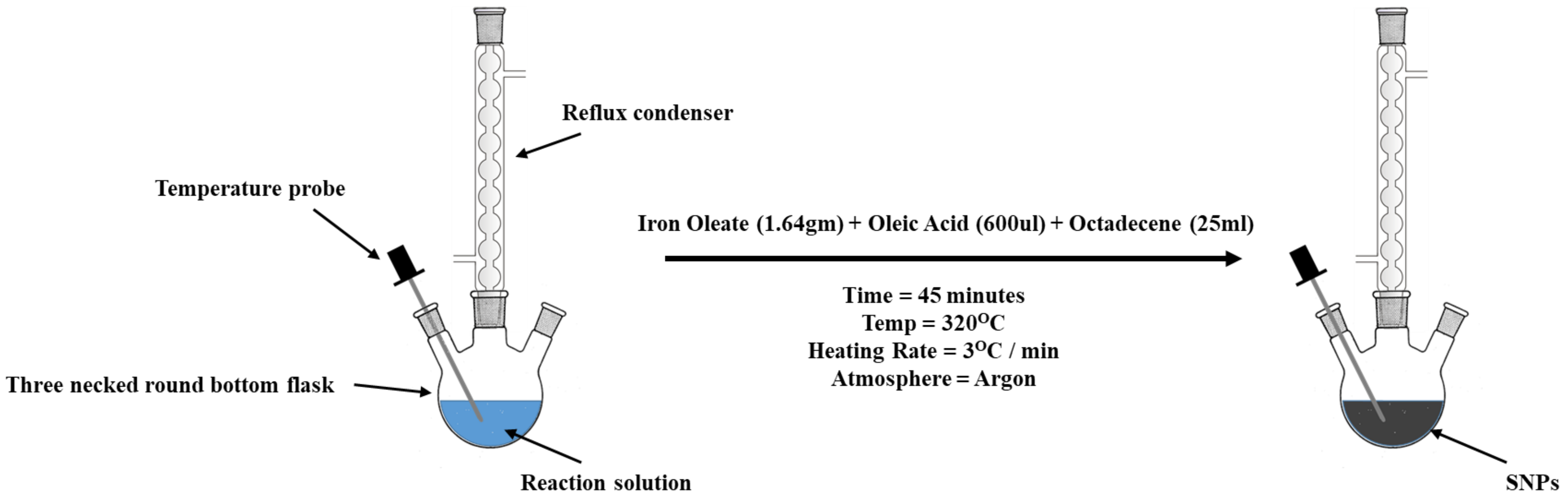




Courtesy: Anuvansh Sharma, PhD Candidate

2. Thermal Decomposition

- Preparation of Metallic Precursor.
- Thermal decomposition of Metallic Precursor.

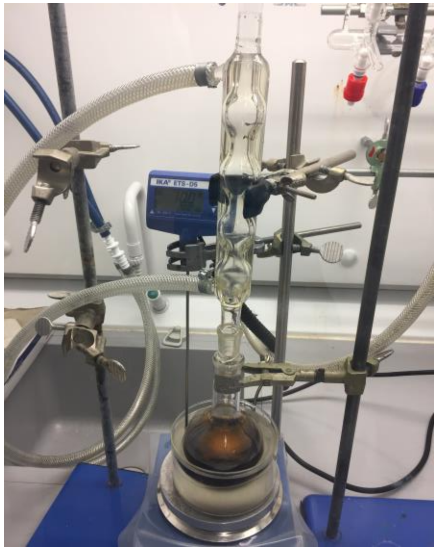


Courtesy: Anuvansh Sharma, PhD Candidate

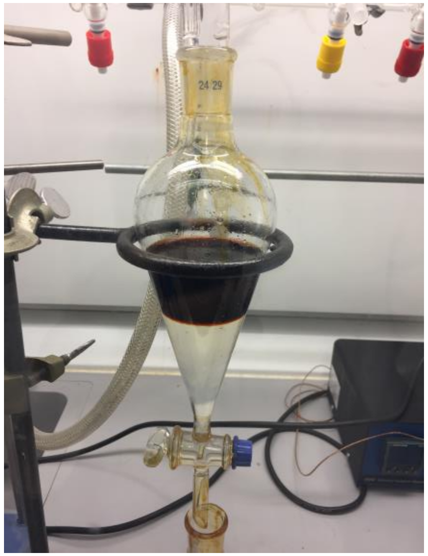
Iron Oxide NPs

Preparation of Metallic Precursor

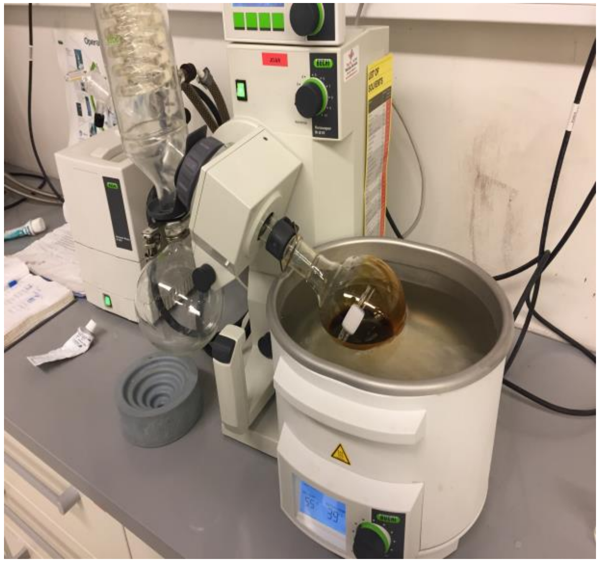
I



II



III

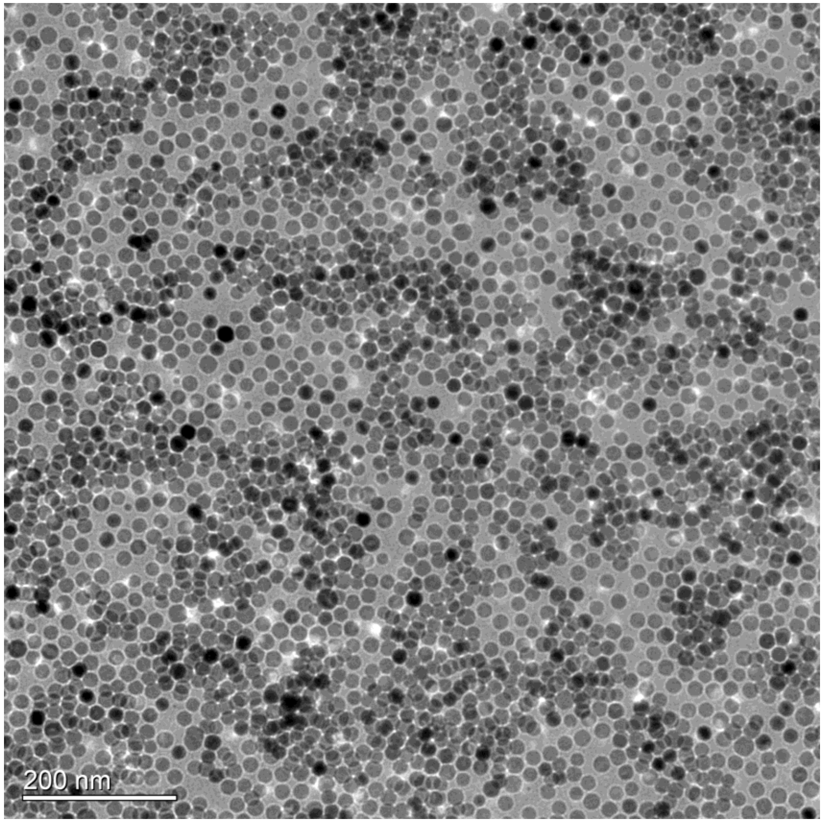


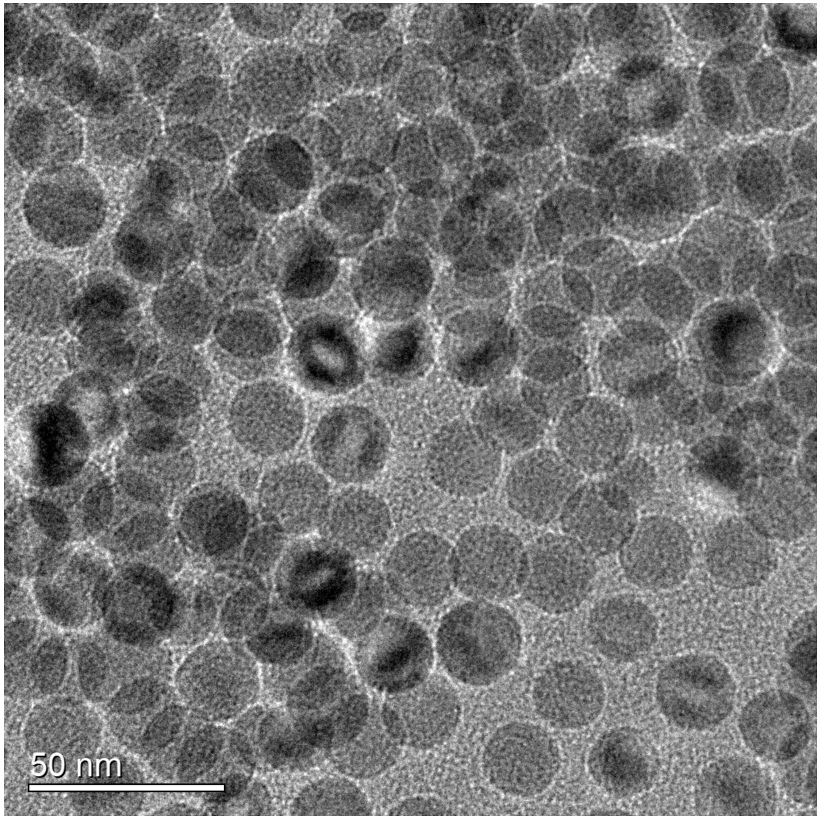
- $FeCl_3.6H_2O$ + Na-Oleate

  Solvents: Water + Hexane + Ethanol
- Mixture is refluxed at $70^{O}C$ for 4 hours with vigorous stirring. (Fig I)
- Red organic phase washed with water. (Fig II)
- Evaporation of solvent. (Fig III)

Courtesy: Anuvansh Sharma, PhD Candidate

Iron Oxide NPs

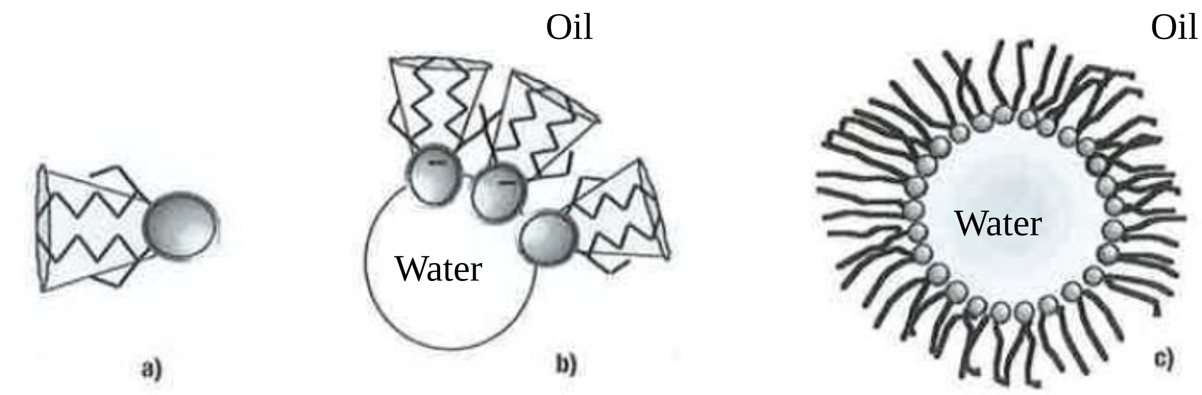




Courtesy: Anuvansh Sharma, PhD Candidate

3. Colloidal Templating: Reverse Micelles as Spherical Nanoreactors

Formation of reverse micelles



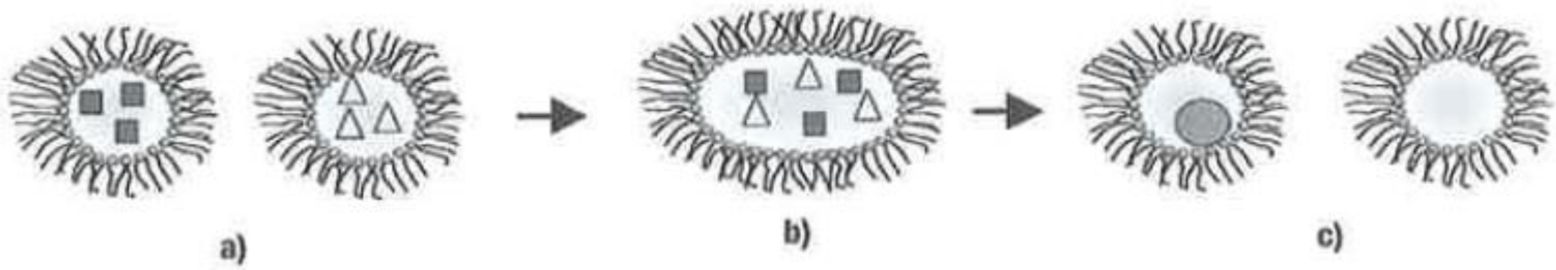
Surfactant with small polar head and acyl chains

Surfactants join together in non-polar solvents…

..forming reverse micelles

Often microemulsions

General principle: Exchange of aqueous cores



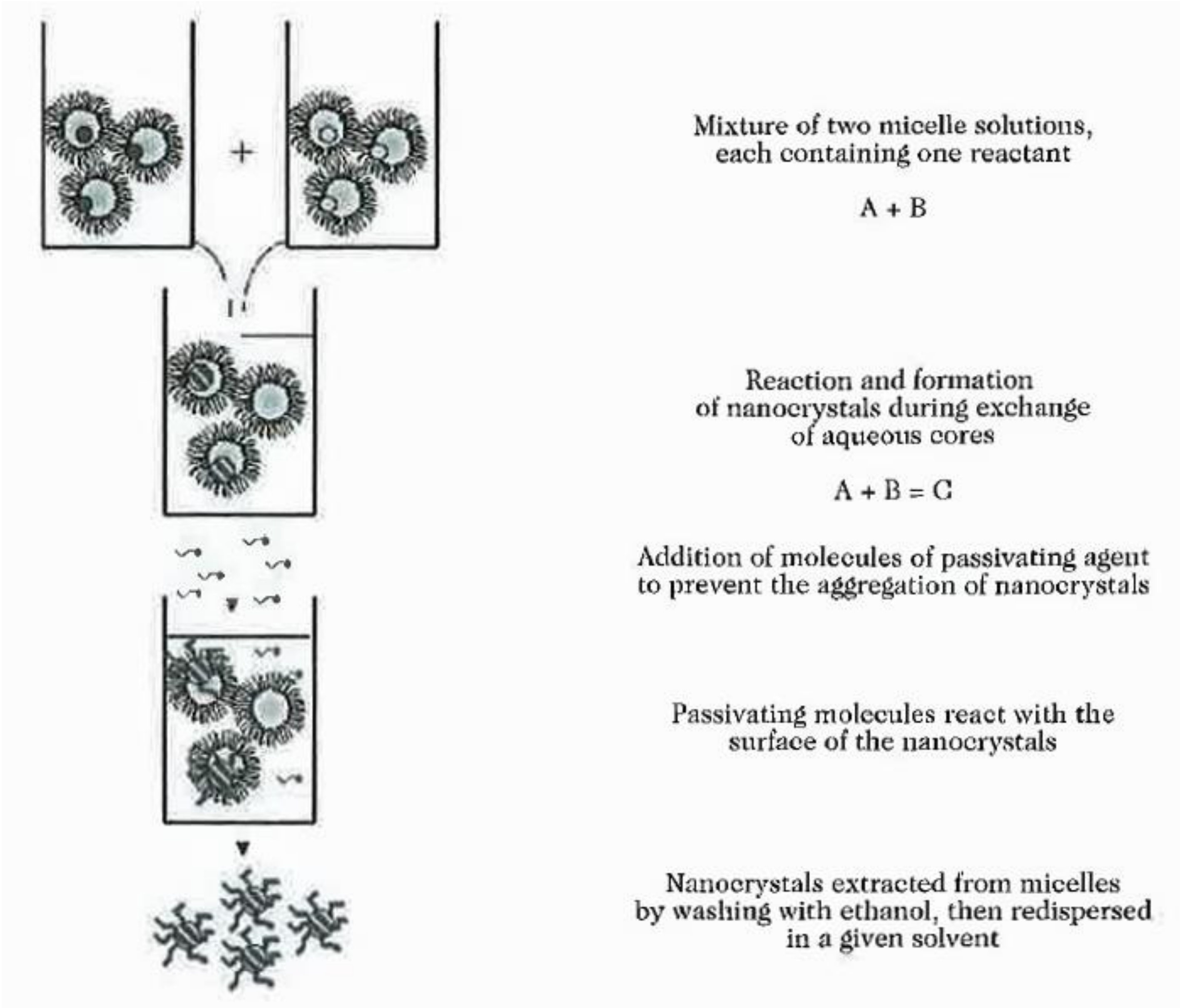
Reverse micelles subject to Brownian motion

Collapsed reverse micelles and mixing of aqueous content

Formation of two micelles, identical to the initial micelles

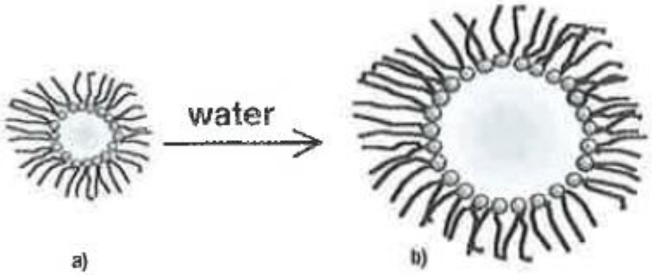
■ Metal precursor

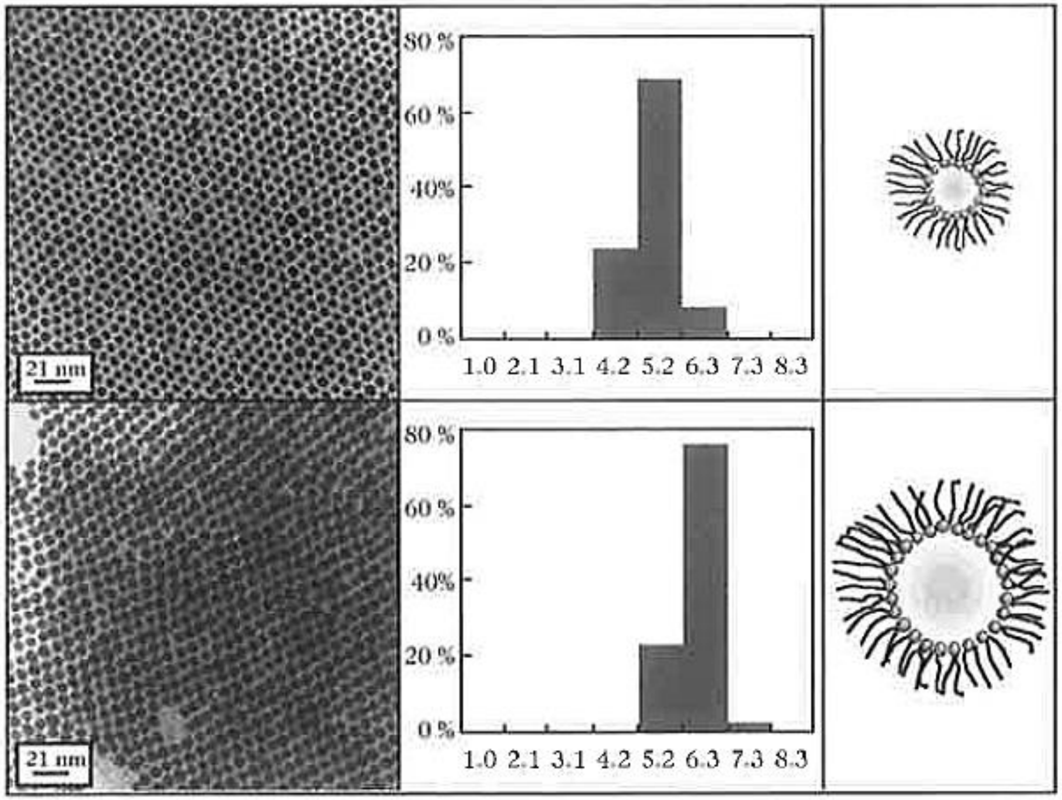
△ Reducing agent



Bréchignac C, Houdy P, Lahmani M. Nanomaterials and Nanochemistry;Springer, 2006.

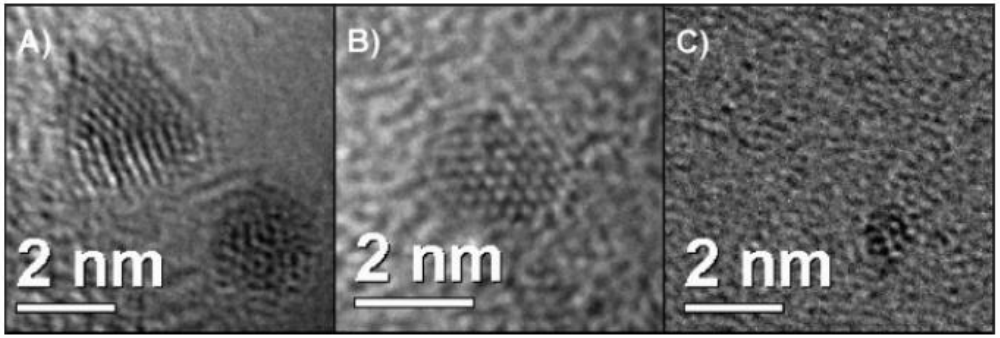
Controlling the size of the reverse micelles controls the size of the nanoparticles, as shown here for silver nanocrystals

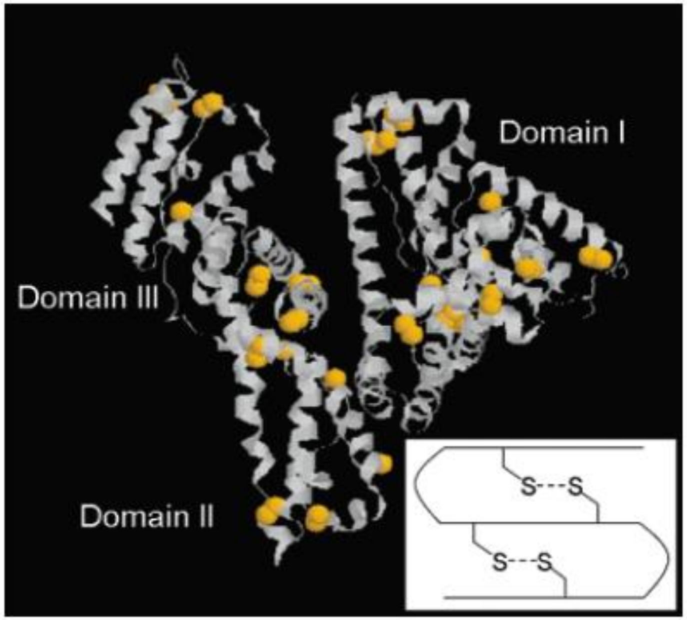




4. One-pot Synthesis Using Globular Proteins

$HAuCl_4$ + $NaBH_4$ (reducing agent) + Bovine Serum Albumin (BSA)

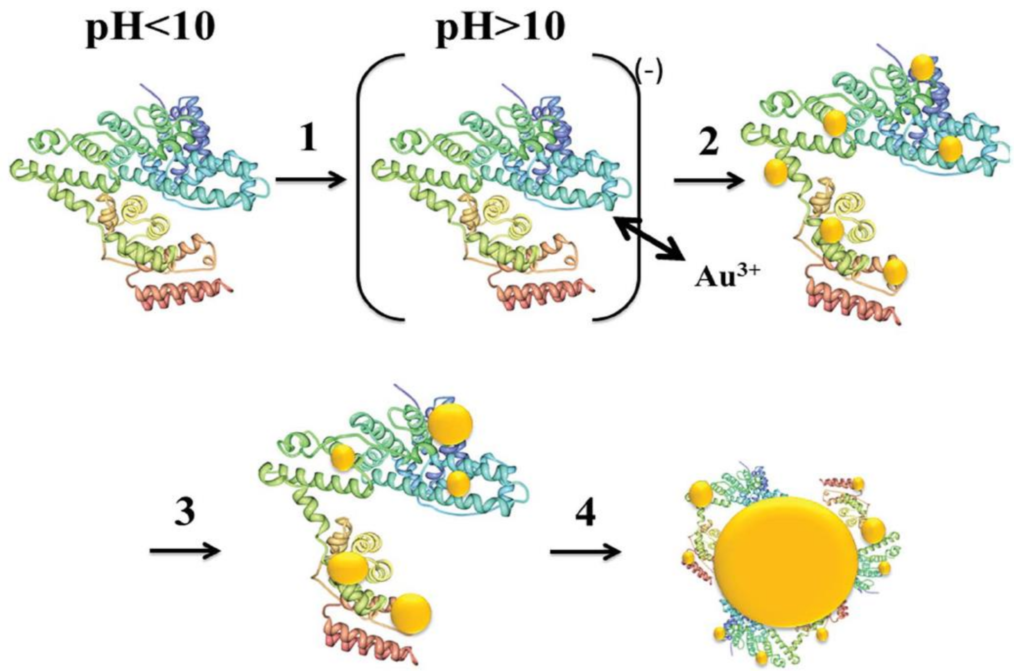




Au NPs embedded in the protein

Burt, J.L. et al., *Langmuir*, **2004**, 20, 11778-11783

One-Pot Synthesis Using Globular Proteins



Proposed mechanism for growth of AuNPs stabilized by BSA.

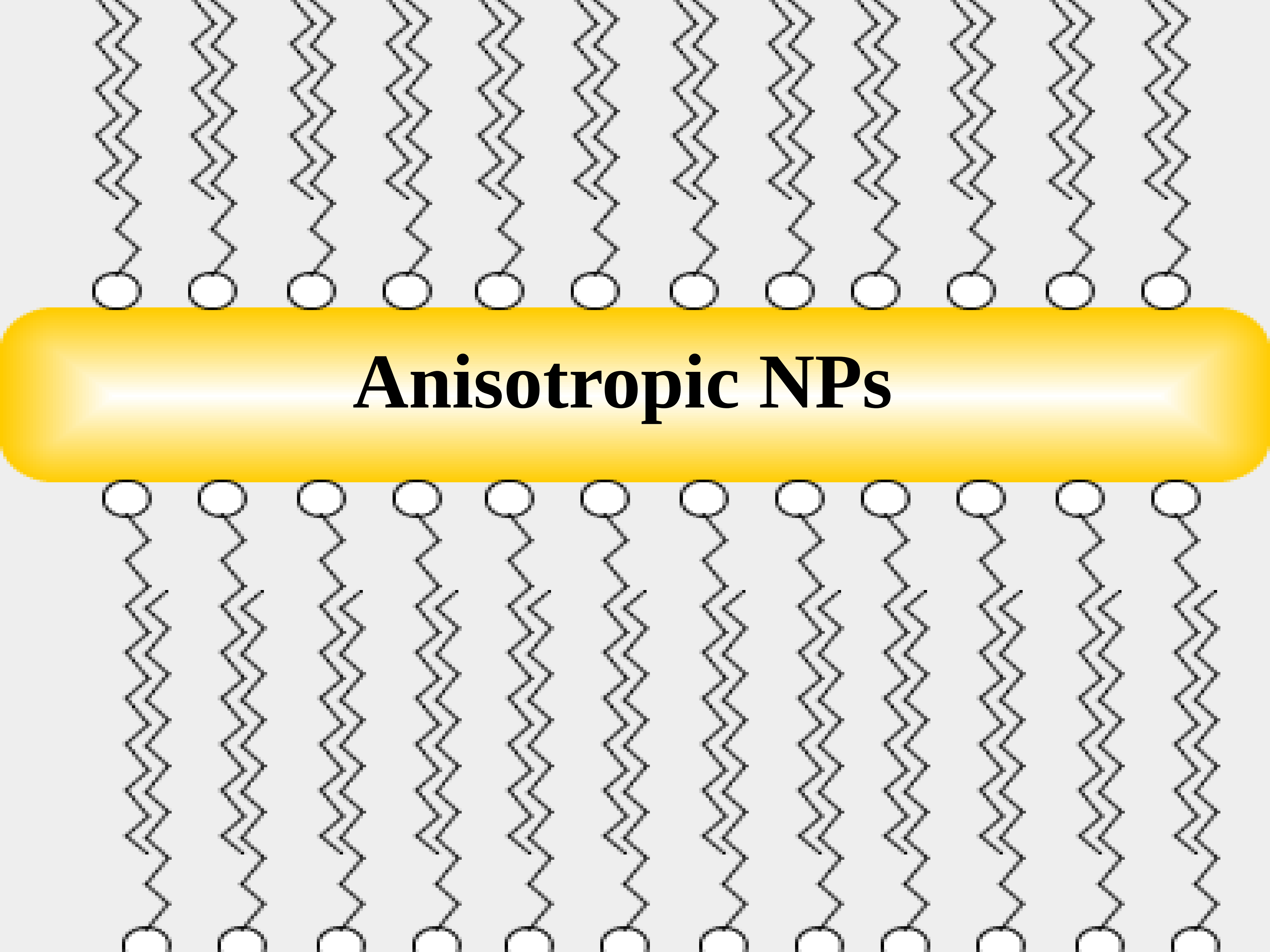
1. Increasing the pH to above 10 causes BSA to be negatively charged which induces electrostatic interactions with the gold ions.

2. Vis AuNCs that emit in the visible region of the EM spectrum start to form.

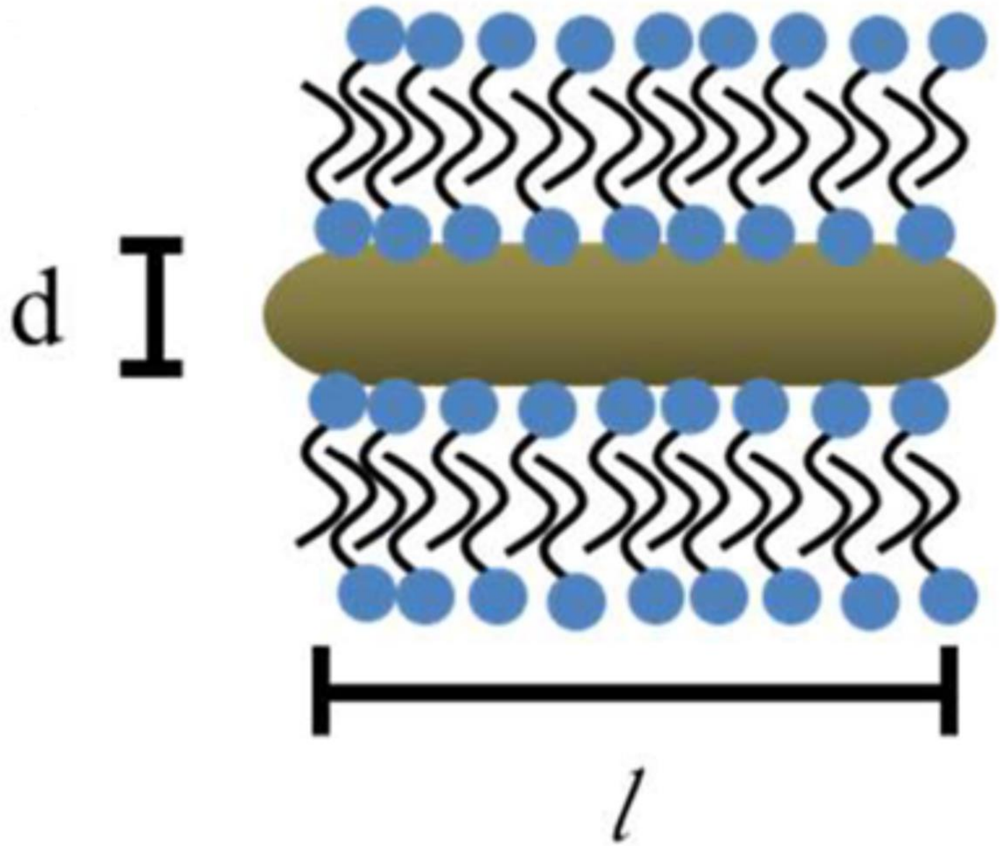
3. Depending on time and concentration of $HAuCl_4$, larger Near IR AuNCs.

4. AuNPs are formed via a shuffling of Near IR AuNCs.

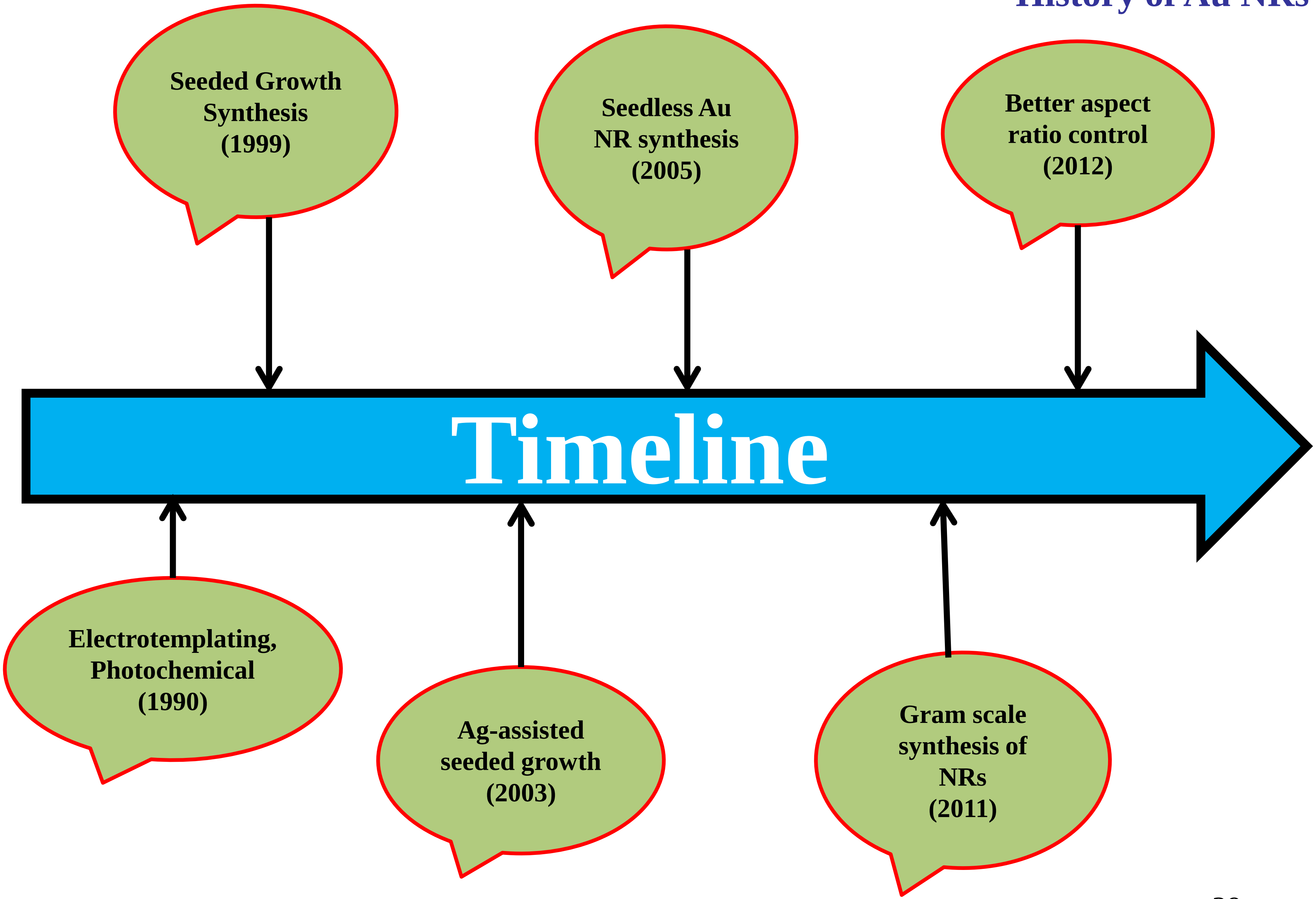
McDonagh, B.H. et al., *RSC Advances*, **2015**, 5, 101101–101109


Anisotropic NPs

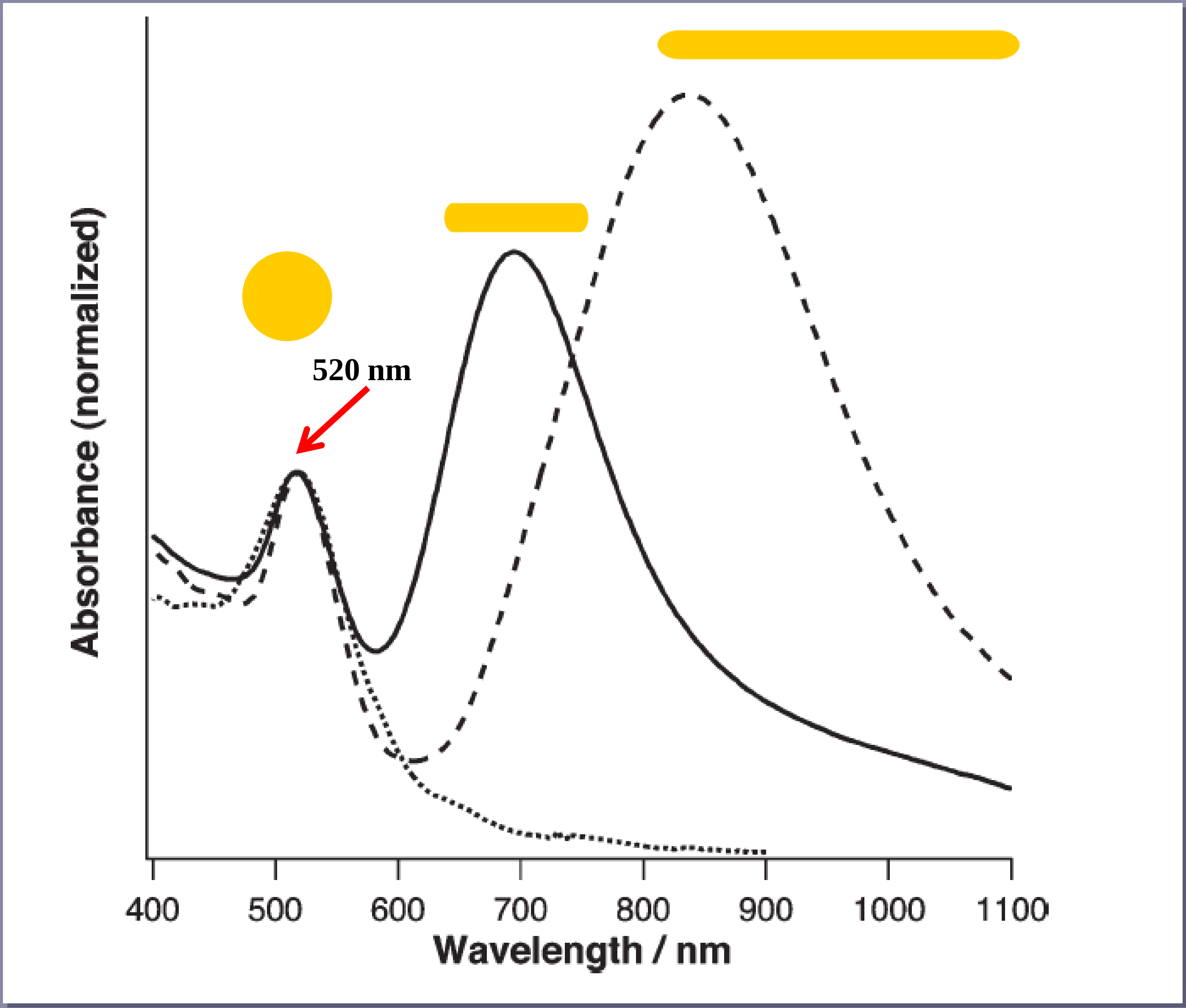
Aspect Ratio



Aspect Ratio = l/d


Timeline
Electrotemplating, Photochemical (1990)
Seeded Growth Synthesis (1999)
Ag-assisted seeded growth (2003)
Seedless Au NR synthesis (2005)
Gram scale synthesis of NRs (2011)
Better aspect ratio control (2012)

Localized Surface Plasmon Resonance (LSPR)

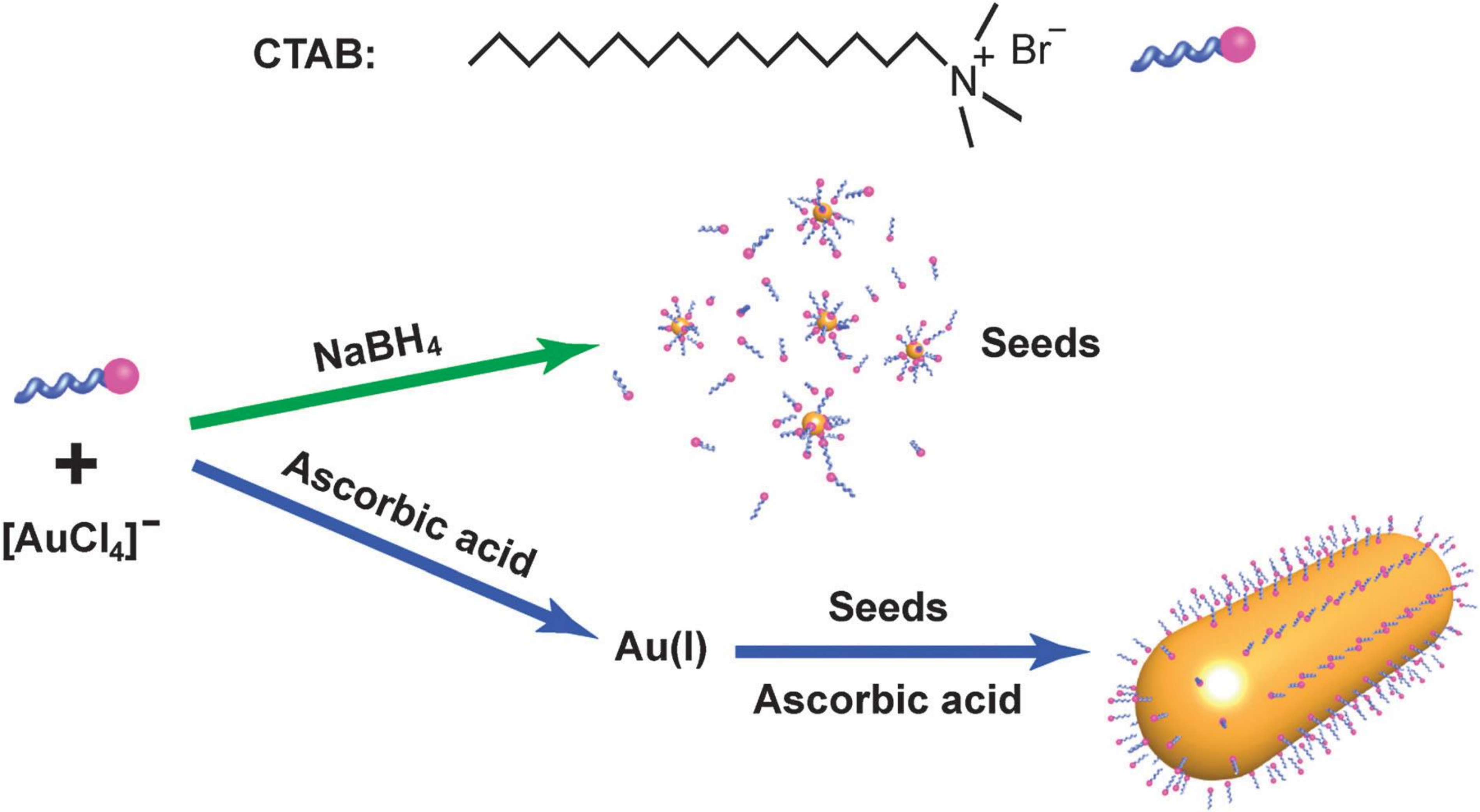


Okamoto et al., *J. Mater. Chem.*, 2006,3920-3928

VS

Larger extinction coefficient (ε)	**Smaller** extinction coefficient (ε)
Scatter **more** light at longitudinal plasmon λ	Scatter **less** light at longitudinal plasmon λ
Better performance in optical imaging	Improved efficiency in photothermal applications

Seeded Growth Synthesis (In a Nutshell)



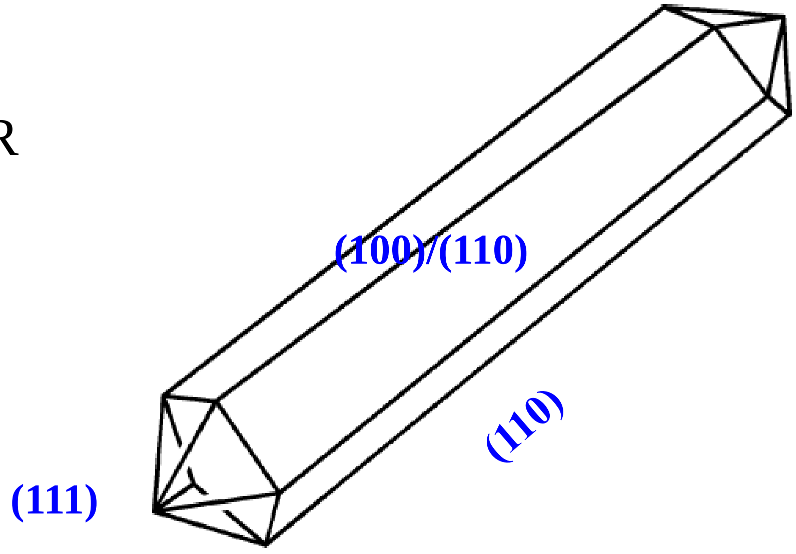
Wang et al, *Chem. Soc. Rev.*, **2013**, 42, 2679

Factors

- Size and surface chemistry of the seed

Size increases, decrease in AR

Surface charge effects dispersity of AR



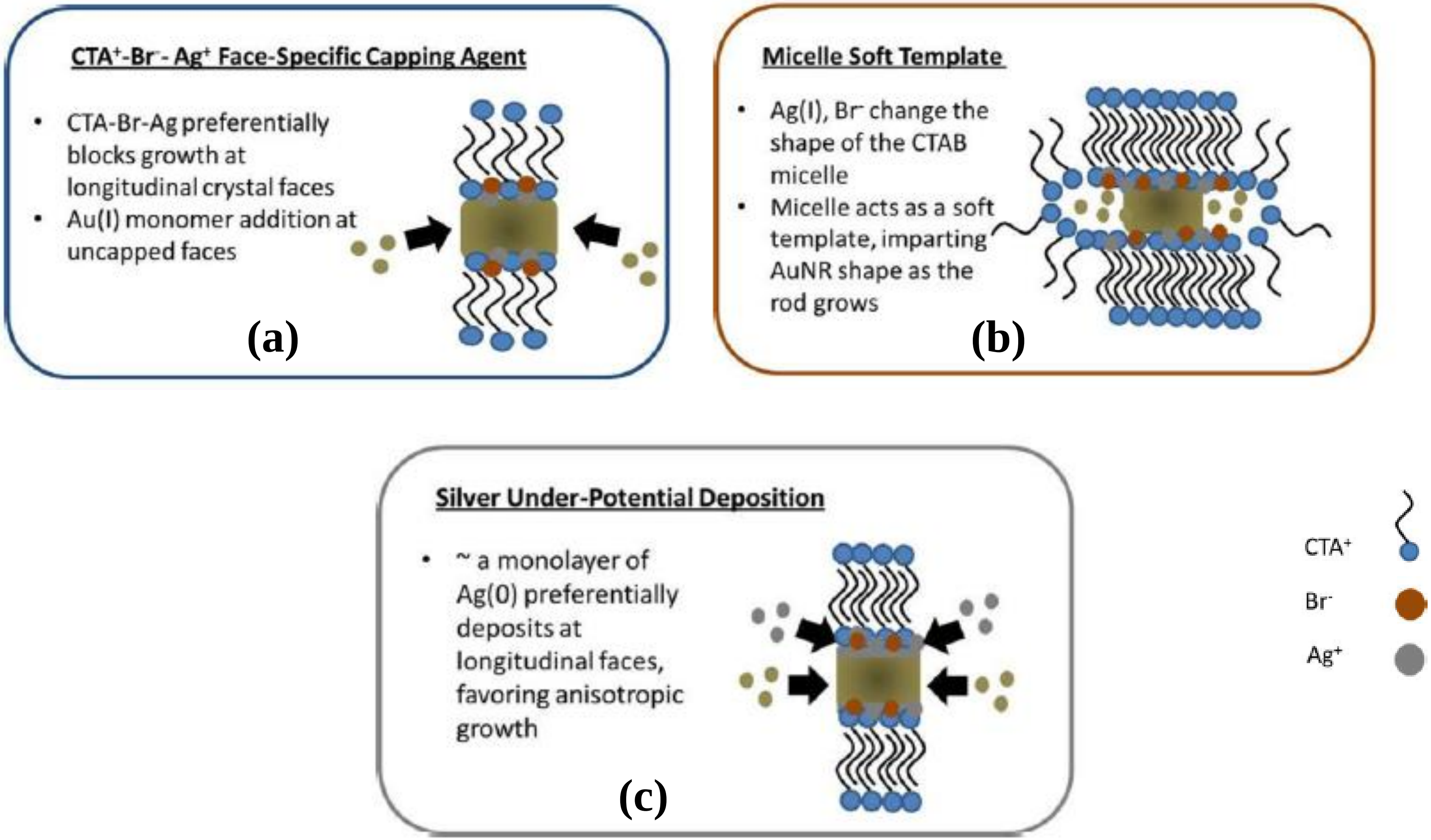
- Chain length of the directing agent

Length< CTAB, lower AR

- Nature of the counterion

Cl^- growth is inhibited

Growth Mechanism

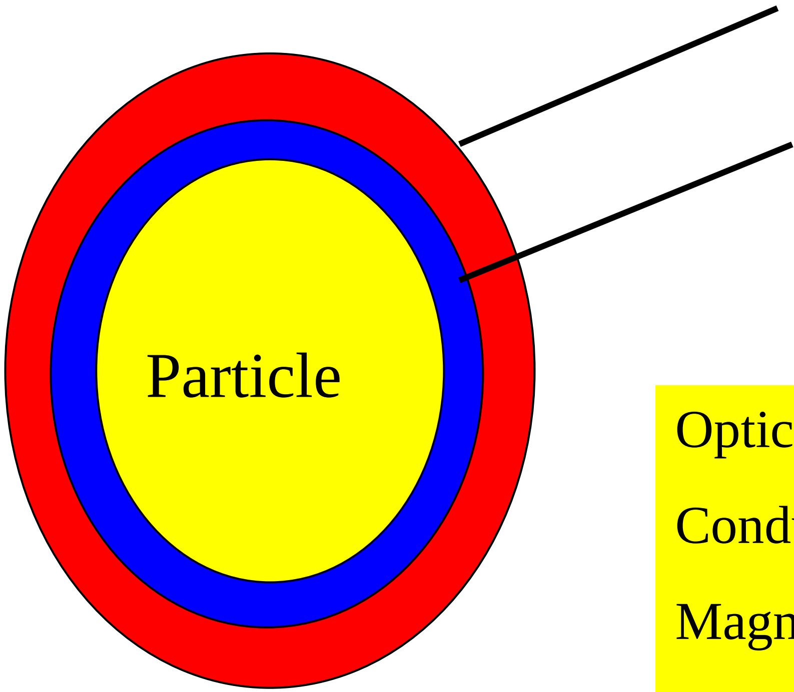


Murphy et al, *Chem*, *Mater.*, **2013**,1250-1261

Functionalization of NPs

Functionalization – Why?

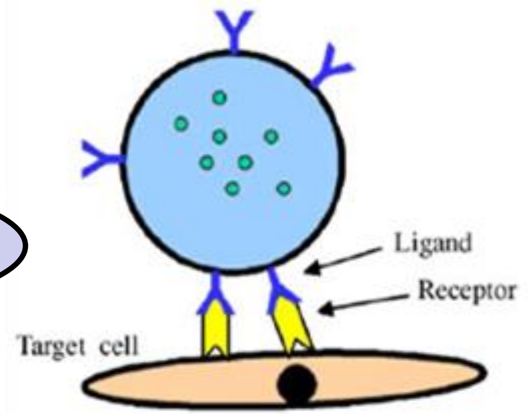
- Ag and Au NPs are not stable in solutions without a surface layer of a passivating ligand
- This imparts an electrostatic and/or steric stabilization to the colloidal sol.



Optical properties	Refractive index
Conductivity	Polarity/solubility
Magnetism	Charge
Catalytic activity	Functionality

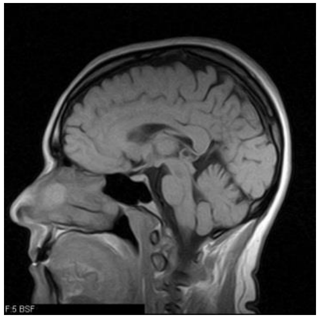
Functionality/application

Functionalization – Why?



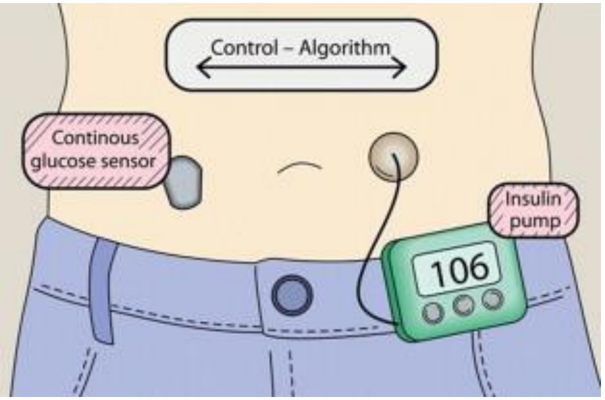
Drug Delivery

Imaging



Catalysis

Biosensors



Environmental Applications

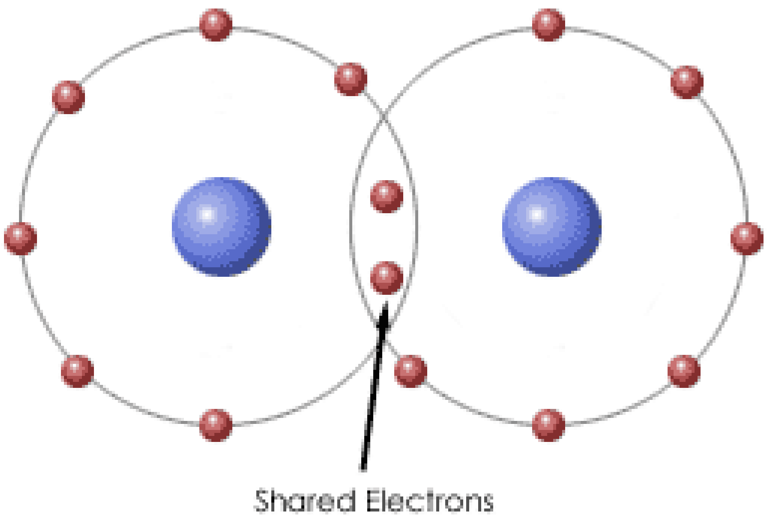
And many more…

Approaches to Functionalization

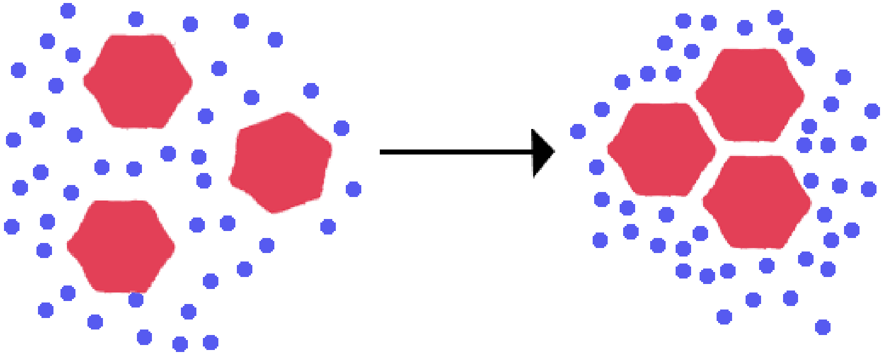
1. **Direct (*in situ*) Functionalization**
    - Done during synthesis
    - Examples:
        - Turkevich Reaction
        - Brust Reaction
2. **Post - Synthesis Functionalization**
    - Functionalization after synthesis
    - Factors
        - Binding to or replacing the exisiting surface ligand
        - Intermolecular forces
        - No of attachment sites, thickness and density of surface layer
        - No. of different surface groups required

Approaches to Functionalization
Post - Synthesis Functionalization

- Examples:
  - Non – specific binding
  - Displacement
  - Layer – by – layer (LBL)
  - Protein binding
  - Grafting polymers, etc.



Covalent



Hydrophobic

Reader's Digest Version:

- Huge library of NPs of different shapes and sizes can be synthesized using solution methods.
- Metallic Precursor + Reducing Agent + Passivating Ligand.
- Strength of the reducing agent controls particle size.
- Synthesis strategy dependent on:
  - Properties of NPs desired.
  - Simplicity of the process.
  - Further application downstream.
- Control of particle size – supersaturation, nucleation, growth.